A Versatile Palladium Catalyzed Approach to Acyl Fluorides and Carbonylations by Combining Visible Light and Ligand Driven Operations

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Supporting Information

1. General materials and methods

All manipulations were conducted in a glovebox under a nitrogen atmosphere. All reagents were purchased from commercial sources, unless otherwise noted. Prior to use in catalysis, all liquid substrates were degassed, transferred to a glovebox, and dried with 4Å molecular sieves. Solid reagents were transferred to a glovebox under nitrogen, dissolved in dichloromethane, stirred over 4Å molecular sieves, then filtered and the solvent removed *in vacuo*. Solvents were dried by filtration through 4Å molecular sieves under nitrogen on an MBraun solvent purification system, and then stored over activated 4Å molecular sieves inside the glovebox. Deuterated acetonitrile and benzene were stirred over calcium hydride, vacuum transferred, degassed, and stored over 4Å molecular sieves. The precursor to (DPE-Phos)Pd$(CO)_2$, [(DPE-Phos)Pd]$_2$(μ-CO), was prepared according to previously reported procedures and stored at -35 °C in the glovebox to avoid decomposition.[1] Research grade carbon monoxide (99.99%) was used as received. Warning: CO is a poisonous gas that requires all the experiments to be conducted in well-ventilated fume hoods. For reactions performed in a J-Young NMR tube, carbon monoxide was added by attaching the J-Young tube to a schlenk line of a known internal gas volume (67 mL) and equipped with a pressure gauge. The NMR tube solution was frozen in liquid nitrogen, the headspace evacuated, the tube closed, and the schlenk line was filled with 800 mTorr of CO. In order to condense 4 atm CO into the 2.2 mL headspace of the NMR tube, the tube was opened until a pressure drop of 120 mTorr was recorded on the schlenk line (corresponding to 0.44 mmol of CO; which equals 4 atm CO in the J-Young NMR tube based on the idea gas law). For reaction in Schlenk bombs at 1 atm CO, the solution was frozen in liquid nitrogen, evacuated, thawed, and the tube was pressurized to 1 atm CO. For reaction in Schlenk bombs at 4 atm CO, 4 atm CO was added to the existing atmosphere of nitrogen.

Kessil 40W A160WE Tuna Blue LED lamps were purchased from Reef Supplies. Nuclear magnetic resonance (NMR) characterization was performed on 400, 500 or 800 MHz spectrometers for proton, 126 or 201 MHz for carbon, 162 MHz for phosphorus and 377 or 471 MHz for ^{19}F NMR. ^{1}H and ^{13}C NMR chemical shifts were referenced to residual solvent. Mass spectra were recorded on a high-resolution electrospray ionization quadrupole mass spectrometer. Electrochemical potential was obtained with a CHI720C potentiostat from CH-instrument in a three electrode cell.

2. Supplementary Figures

Electrochemical potential of benzoyl fluoride was obtained with a CHI720C potentiostat from CH-instrument. Samples were prepared with 0.06 mmol (0.001 M) of benzoyl fluoride in 6 mL of a 0.1 M $^{n}Bu_4NPF_6$ solution in dry, degassed acetonitrile. Measurements employed a pre-polished glassy carbon working electrode, platinum wire counter electrode and a silver wire as a pseudo-reference electrode. The scan rate was 100 mV/s and the data were adjusted versus ferrocene as an internal standard. Half-peak potential: $E_{p/2}$ = -2.29 V *vs* ferrocene, or an estimation of $E_{p/2}$ = -1.89 V *vs* SCE.[3-4]

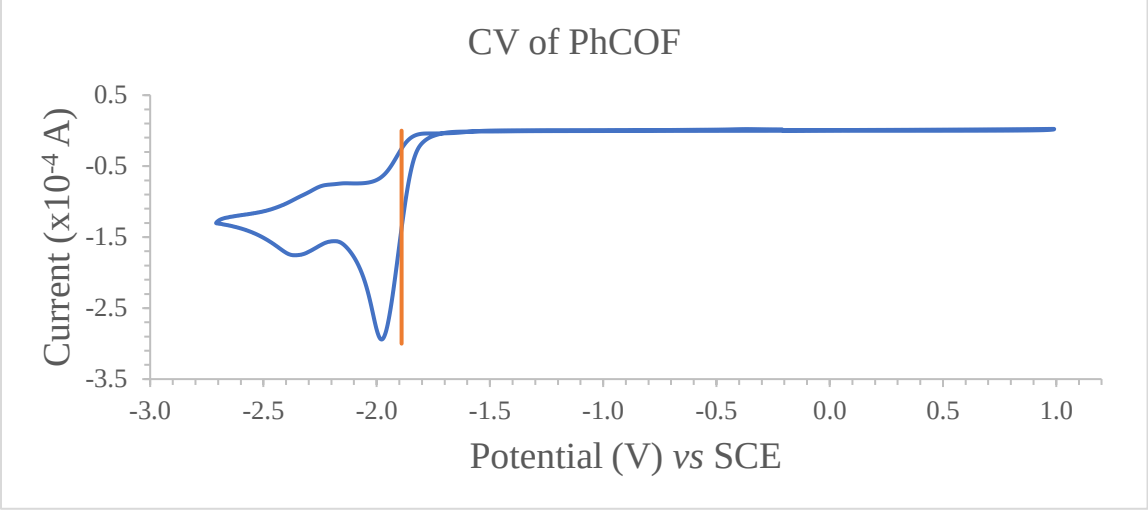


Figure S1. Cyclic voltammogram of benzoyl fluoride.

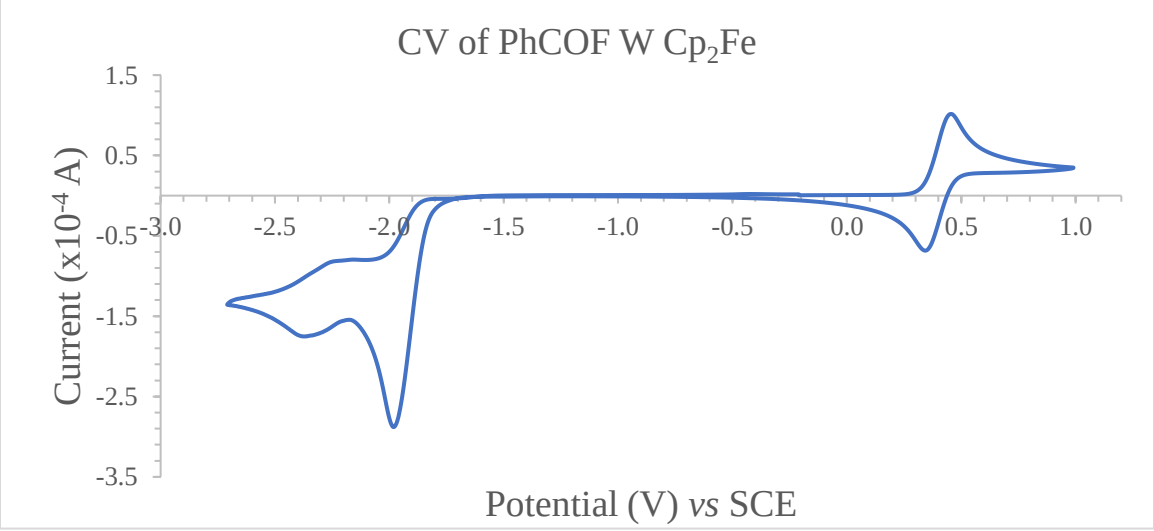
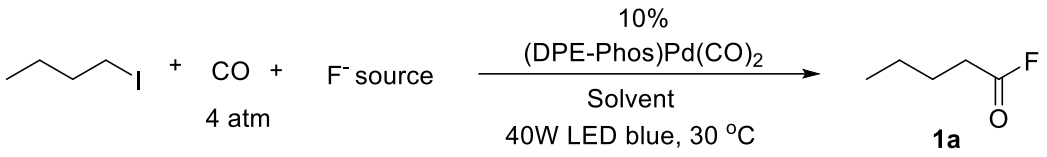


Figure S2. Cyclic voltammogram of benzoyl fluoride in the presence of Cp_2Fe.



Entry	*Solvent*	*F⁻ source*	*Yield*
1	MeCN	AgF	23%
2	MeCN	ZnF_2	4%
3	MeCN	CsF	49%
4	MeCN	KF	74%
5	DCE	KF	20%
6	THF	KF	18%
7	Benzene	KF	0%

Figure S3. Fluoride source and solvent influences on acyl fluoride formation.

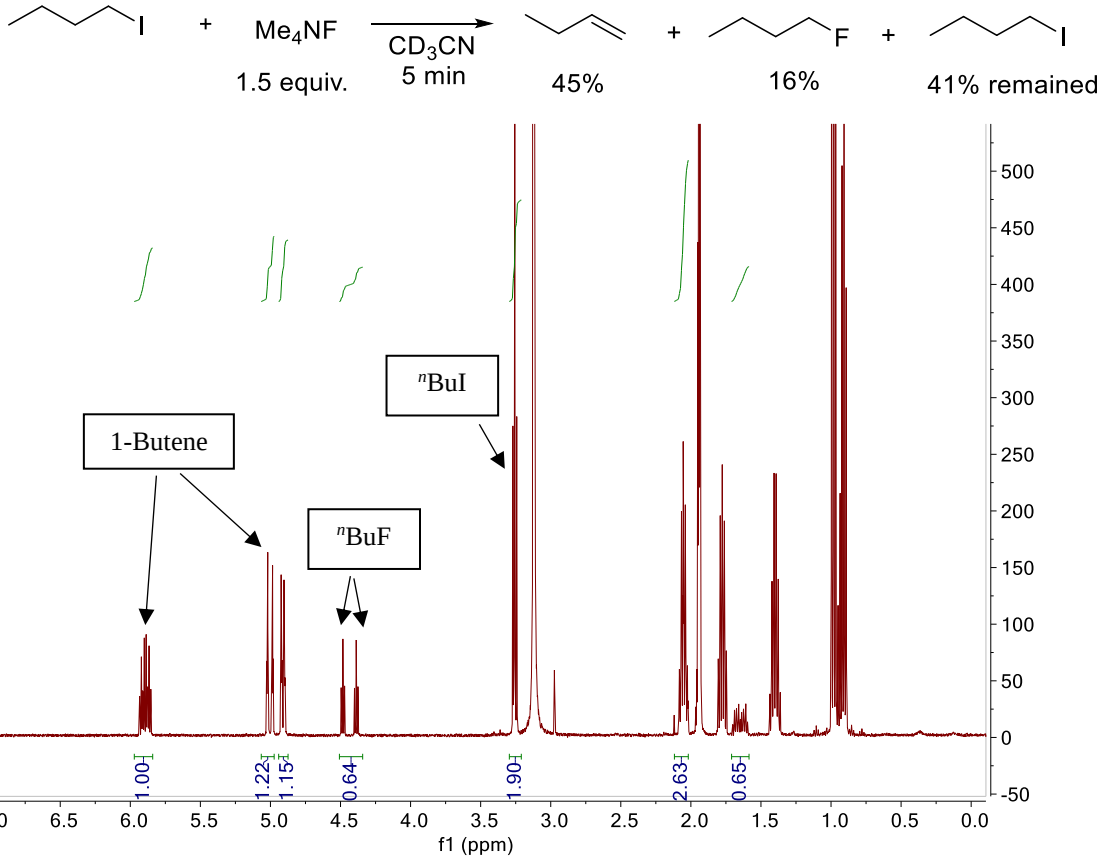
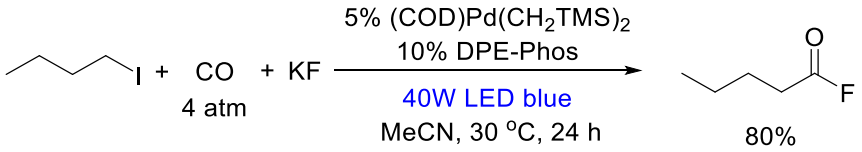


Figure S4 The reaction of *n*-butyl iodide and Me_4NF.

3. Typical procedure for reaction development (Figure 2)



In a glovebox, *n*-butyl iodide (18.4 mg, 0.10 mmol), (COD)Pd($CH_2TMS)_2$ (1.9 mg, 0.0050 mmol), DPE-Phos (5.4 mg, 0.010 mmol) and benzyl benzoate standard (4.2 mg, 0.020 mmol) were dissolved in 2 mL of CH_3CN. The mixture was transferred into a thick-walled 25 mL glass reaction vessel equipped with a magnetic stir bar and a Teflon cap. A suspension of potassium fluoride (11.6 mg, 0.20 mmol) was prepared in 1 mL CH_3CN and transferred to the vessel. The vessel was closed, taken out of the glovebox and attached to a CO line. Before opening the vessel, the connecting tubing was evacuated and backfilled with carbon monoxide three times, and finally, the vessel was opened and pressurized with 4 atm carbon monoxide (on top of 1 atm of nitrogen). The vessel was closed and clamped on top of a stirring plate, and the solution was irradiated using a 40W Blue LED lamp. Fans were used to keep the temperature below 30 ºC (see the picture of setup in Figure S5A). After 24 hours, the vessel was taken out of the irradiation system and attached to a Schlenk line. The mixture was frozen by liquid nitrogen, and the excess CO was removed by opening the cap to vacuum. The vessel was brought into the glovebox. An aliquot was taken, and the formation of acyl fluoride **1a** was confirmed *in situ* by ^{1}H and ^{13}C NMR analysis. To confirm the yield of the acid fluoride, benzylamine (21.4 mg, 0.20 mmol) and $EtN^{i}Pr_2$ base (25.9 mg, 0.20 mmol) were added, and the yield of the amide **5a**, 80%, was calculated based on the internal standard.

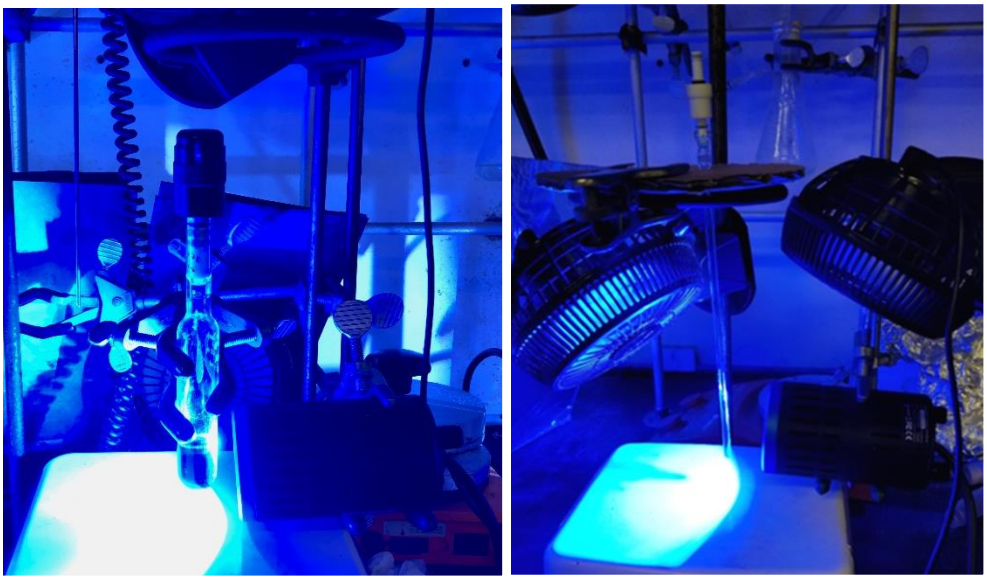
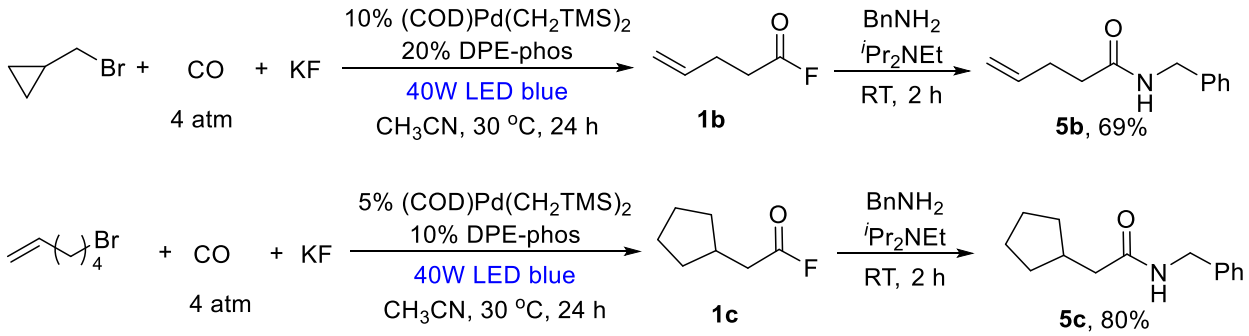


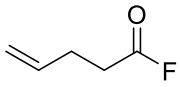
Figure S5. Blue light irradiation setup.

4. Mechanistic studies (Figure 3)

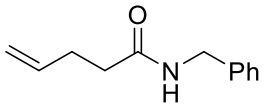
4.1 Radical clock experiments (Figure 3a)



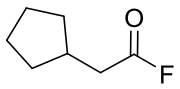
Reactions were performed as described in section 5.1 and 5.2. Acyl fluorides **1b** and **1c** were characterized by *in situ* ^{1}H, ^{19}F and ^{13}C NMR analysis, and isolated by column chromatography upon conversion to amides **5b** and **5c**. Column conditions: Silica gel, gradient hexane/ethyl acetate 20% to 40%, affording amide **5b** as a pale-yellow liquid in 69% yield (26.3 mg, 0.14 mmol), and amide **5c** as a pale-yellow solid in 80% yield (34.9 mg, 0.16 mmol), respectively.



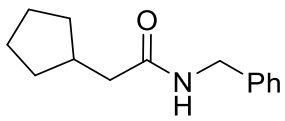
Pent-4-enoyl fluoride (1b). *In situ* ^{1}H NMR (500 MHz, CD_3CN) δ 5.86 (ddt, *J* = 17.3, 10.3, 6.5 Hz, 1H), 5.12 (ddt, *J* = 17.2, 1.7, 1.7 Hz, 1H), 5.05 (ddt, *J* = 10.3, 1.4, 1.4 Hz, 1H), 2.67 (t, *J* = 7.3 Hz, 2H), 2.38 (ddt, *J* = 13.7, 7.4, 1.5 Hz, 2H). ^{13}C NMR (126 MHz, CD_3CN) δ 163.5 (d, *J* = 359.2 Hz), 135.8, 115.7, 31.0 (d, *J* = 50.8 Hz), 27.4 (d, *J* = 2.8 Hz). ^{19}F NMR (377 MHz, CD_3CN) δ 42.95.



***N*-benzylpent-4-enamide (5b)**. 69% yield (26.3 mg, 0.14 mmol). Pale yellow liquid. Spectral data correlated with that previously reported in the literature.[5] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 2H), 7.30 – 7.26 (m, 3H), 5.83 (ddt, *J* = 16.8, 10.2, 6.5 Hz, 1H), 5.75 (s, 1H), 5.07 (ddt, *J* = 17.1, 1.7, 1.7 Hz, 1H), 5.01 (ddt, *J* = 10.2, 1.7, 1.7 Hz, 1H), 4.44 (d, *J* = 5.7 Hz, 2H), 2.46 – 2.37 (m, 2H), 2.33 – 2.29 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.0, 138.3, 137.0, 128.7, 127.8, 127.5, 115.7, 43.6, 35.9, 29.6.

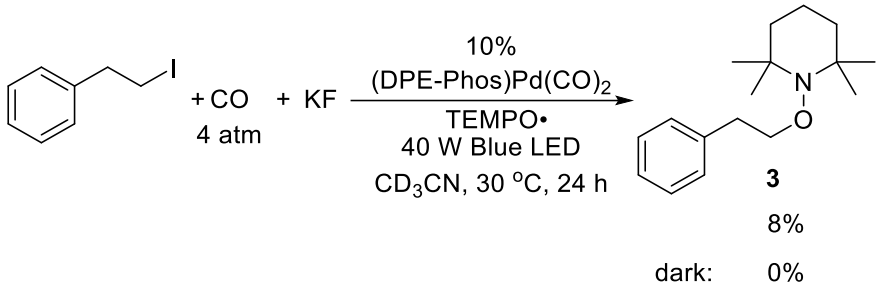


2-Cyclopentylacetyl fluoride (1c) *In situ* ^{1}H NMR (800 MHz, CD_3CN) δ 2.58 (dd, *J* = 7.3, 1.6 Hz, 2H), 2.24 – 2.18 (m, 1H), 1.89 – 1.83 (m, 2H), 1.67 – 1.60 (m, 2H), 1.60 – 1.53 (m, 2H), 1.24 – 1.16 (m, 2H). ^{13}C NMR (201 MHz, CD_3CN) δ 164.1 (d, *J* = 360.0 Hz), 38.0 (d, *J* = 48.4 Hz), 35.9, 32.4, 25.2. ^{19}F NMR (377 MHz, CD_3CN) δ 44.26.



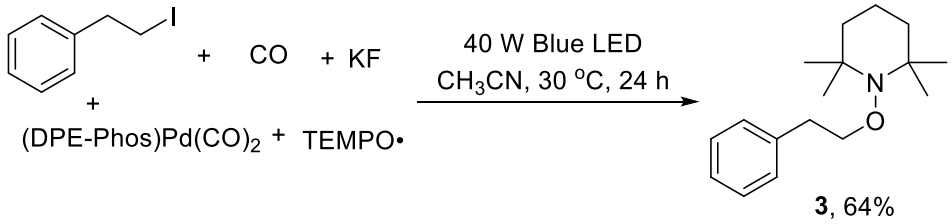
***N*-benzyl-2-cyclopentylacetamide (5c)**. 80% yield (34.9 mg, 0.16 mmol). Pale yellow solid. Spectral data correlated with that previously reported in the literature.[6] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 2H), 7.31 – 7.26 (m, 3H), 5.73 (s, 1H), 4.44 (d, *J* = 5.6 Hz, 2H), 2.33 – 2.23 (m, 1H), 2.24 – 2.19 (m, 2H), 1.89 – 1.80 (m, 2H), 1.68 – 1.52 (m, 4H), 1.21 – 1.10 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.6, 138.5, 128.7, 127.8, 127.5, 43.6, 43.1, 37.2, 32.6, 25.0.

4.2 TEMPO radical trapping experiment (Figure 3a)

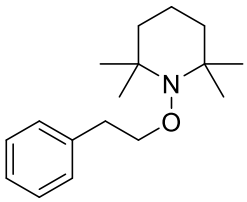


Reactions were performed as described in section 5.1 with (2-iodoethyl)benzene (92.8 mg, 0.4 mmol), [(DPE-Phos)Pd]$_2$(μ-CO) (26.4 mg, 0.02 mmol), potassium fluoride (46.5 mg, 0.80 mmol), TEMPO (62.5 mg, 0.4 mmol), benzylbenzoate standard (2.4 mg, 0.11 mmol) and 12 mL CH_3CN. The yield of TEMPO ether **3**, 8%, was determined by ^{1}H NMR analysis of the crude mixture relative to the internal standard. The TEMPO ether was isolated in an impure form by column chromatography, mixing with excess (2-iodoethyl)benzene as they have similar polarity. Pure compound was isolated in the following stoichiometric reaction. A similar reaction without blue light irradiation led to no TEMPO ether **3**.

Stoichiometric reaction



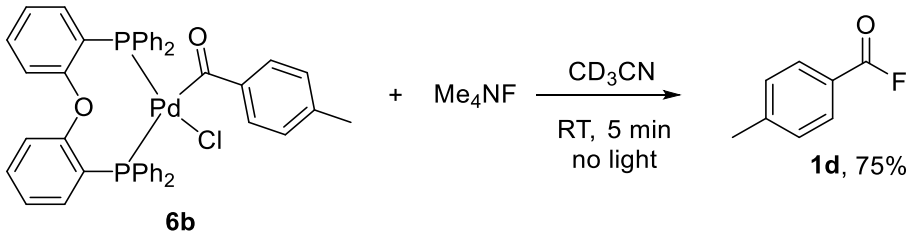
In order to isolate **3**, a similar procedures as described above (section 5.1) was followed using (2-iodoethyl)benzene (9.3 mg, 0.040 mmol), [(DPE-Phos)Pd]$_2$(μ-CO) (26.4 mg, 0.020 mmol), potassium fluoride (46.5 mg, 0.80 mmol), TEMPO (62.5 mg, 0.4 mmol), and 12 mL CH_3CN. The TEMPO ether **3** was isolated by column chromatography: Silica gel, hexane/ethyl acetate 10% affording pure compound **3** as a colorless oil in 64% yield (6.7 mg, 0.030 mmol).



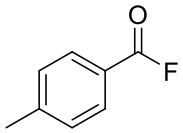
2,2,6,6-Tetramethyl-1-phenethoxypiperidine (3). 64% yield (6.7 mg, 0.03 mmol). Colorless oil. Spectral data correlated with that previously reported in the literature.[7] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 2H), 7.25 – 7.21 (m, 2H), 7.21 – 7.16 (m, 1H), 3.95 (t, *J* = 7.0 Hz, 2H), 2.83 (t, *J* = 7.0

Hz, 2H), 1.48 - 1.59 (m, 1H), 1.48 – 1.38 (m, 4H), 1.35 – 1.24 (m, 1H), 1.07 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.6, 129.1, 128.1, 125.9, 59.7, 39.6, 35.4, 33.0, 20.1, 17.2. HRMS: calculated for $C_{17}H_{28}NO^+$ ($M+H^+$): 262.2165, found: 262.2171.

4.3 The reaction of Pd-acyl complexes with fluoride (Figure 3b)



Complex **6b** was generated based on previously reported procedures.[1] In a glovebox, complex **6b** (3.2 mg, 0.0040 mmol) was transferred into a J-Young NMR tube in 0.55 mL CD_3CN. Me_4NF (0.7 mg, 0.0080 mmol) solution in CD_3CN (0.20 mL) was transferred into the J-Young NMR tube, and the tube was sealed and brought out of the glovebox. After 5 min, ^{1}H NMR analysis shows the disappearance of complex **6b** and the formation of acyl fluoride **1d** in 75% yield, calculated relative to the tetrabutylammonium signal. The acid fluoride was characterized *in situ* by ^{1}H and ^{19}F NMR analysis.



4-Methylbenzoyl fluoride (1d). Spectral data correlated with that previously reported in the literature.[8] *In situ* NMR (500 MHz, CD_3CN) δ 7.94 (d, J = 8.3 Hz, 2H), 7.42 (d, J = 4.7 Hz, 2H), 2.44 (s, 3H). ^{19}F NMR (471 MHz, CD_3CN) δ 15.95.

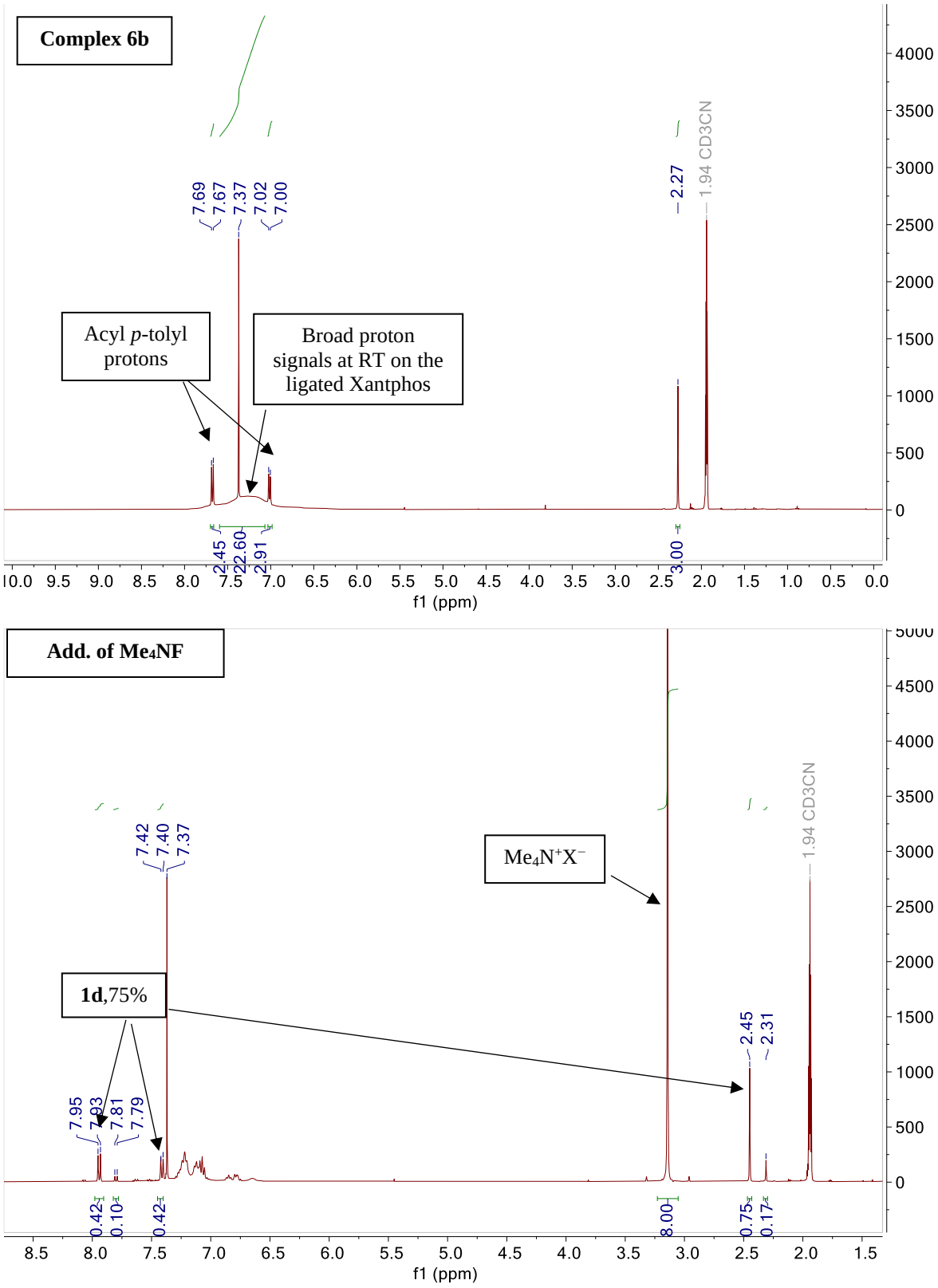


Figure S6. ^{1}H NMR spectra of the reaction of complex 6b and Me_4NF.

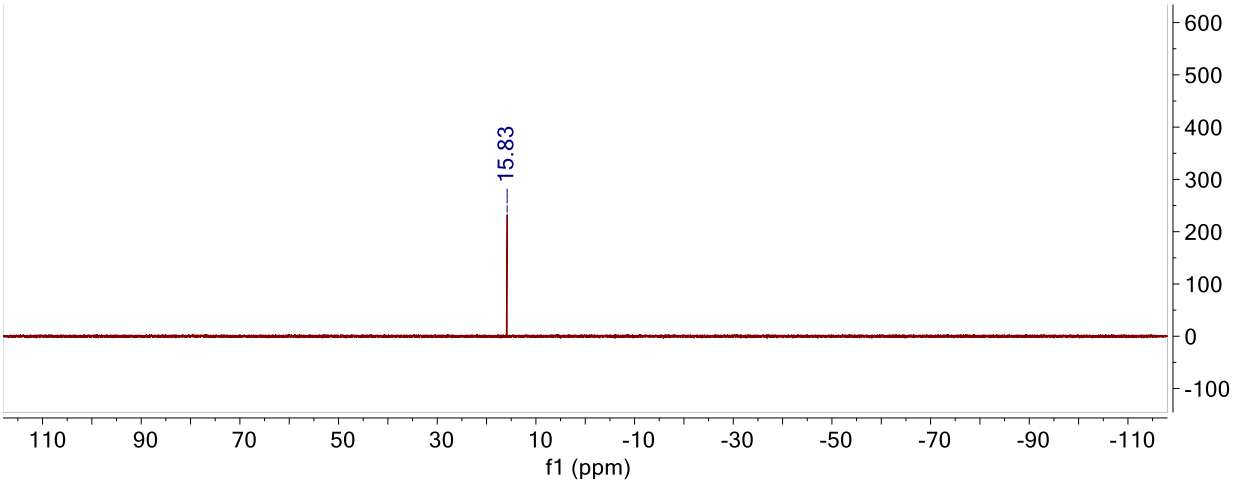
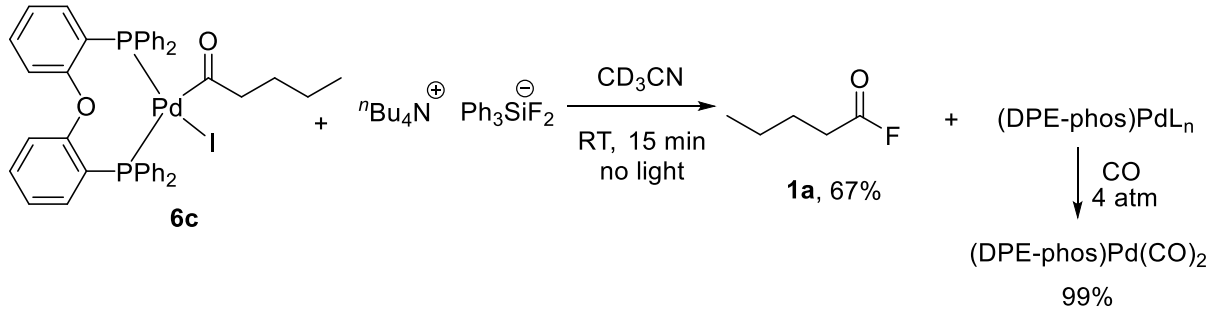
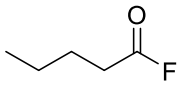


Figure S7. ^{19}F NMR spectra of the reaction of complex 6b and Me_4NF.



Complex **6c** was generated based on previously reported procedures.[1] In a glovebox, complex **6c** (2.6 mg, 0.0030 mmol) and 1,2-dichloroethane standard (0.4 mg, 0.0038 mmol) were mixed with 0.55 mL CD_3CN and transferred into a J-Young NMR tube. The sample was sealed, and an initial ^{1}H NMR was taken. The sample was brought back to the glovebox and placed in a freezer at -30 °C for 5 minutes. Tetrabutylammonium difluorotriphenylsilicate (TBDS) (2.4 mg, 0.0050 mmol) solution in CD_3CN (0.20 mL) was transferred into the J-Young NMR tube, and the tube was sealed and quickly brought out of the glovebox and froze in liquid N_2. The sample was allowed to warm up to room temperature and quickly placed into a 400 MHz NMR spectrometer. After 15 min, ^{1}H NMR analysis showed the disappearance of complex **6c** and the formation of acyl fluoride **1a** in 67% yield, along with dark solid formed on the bottom. The acid fluoride was characterized by *in situ* ^{1}H, ^{19}F and ^{13}C NMR analysis. The tube was frozen under liquid nitrogen. The headspace was evacuated, and then 4 atm of CO were condensed into the tube. (As noted in

the general procedures, this was accomplished by condensing 120 mTorr of a CO filled vacuum line (67 mL volume) into the NMR tube (headspace 2.2 mL)). The sample was mixed by placing it upside down, which resulted in a light purple homogenous solution. ^{1}H NMR analysis showed the formation of 99% of complex (DPE-Phos)Pd(CO)$_2$, **6a**, and ^{31}P NMR analysis showed a single peak at 6.12 ppm, corresponding to complex **6a**.



Pentanoyl fluoride (1a). *In situ* NMR data: ^{1}H NMR (500 MHz, CD_3CN) δ 2.56 (td, *J* = 7.4, 0.7 Hz, 2H), 1.66 – 1.56 (m, 2H), 1.43 – 1.32 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, CD_3CN) δ 164.1 (d, *J* = 359.1 Hz), 31.3 (d, *J* = 50.0 Hz), 25.6 (d, *J* = 2.4 Hz), 21.4, 12.8. ^{19}F NMR (471 MHz, CD_3CN) δ 43.06.

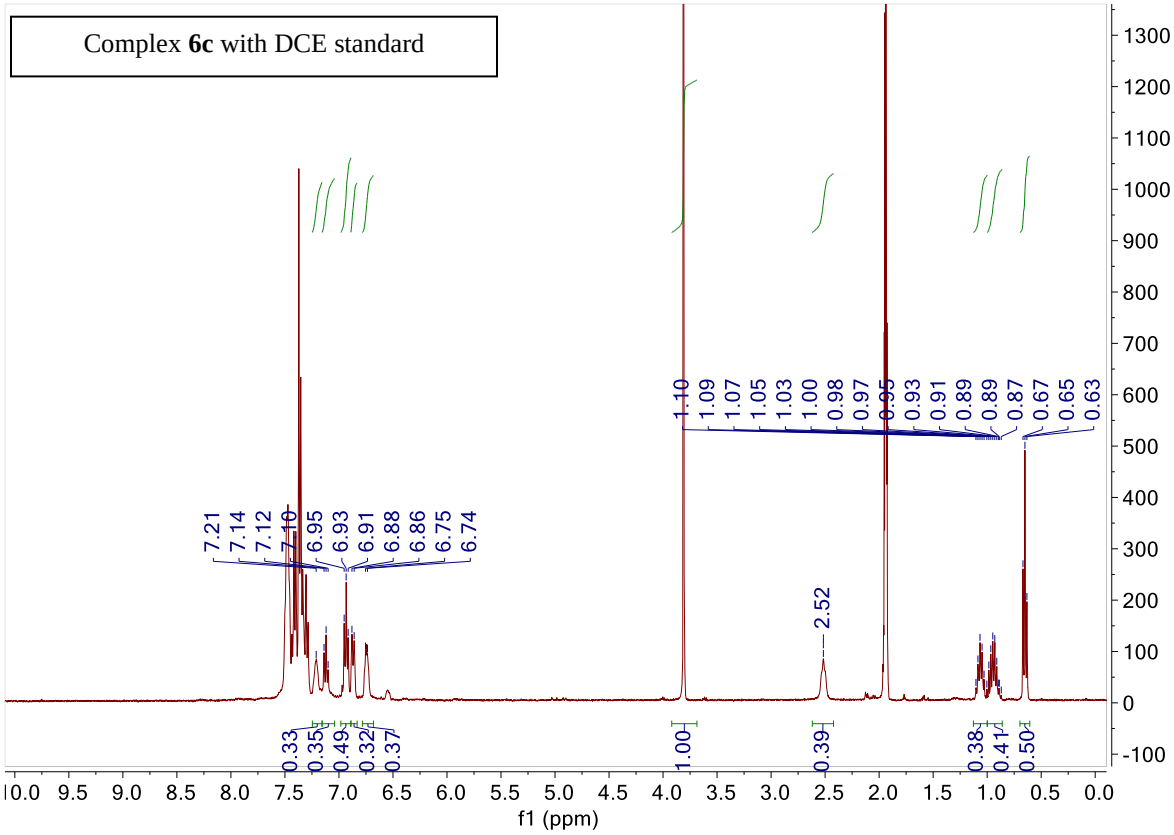


Figure S8. Initial ^{1}H NMR spectra of complex 6c with DCE.

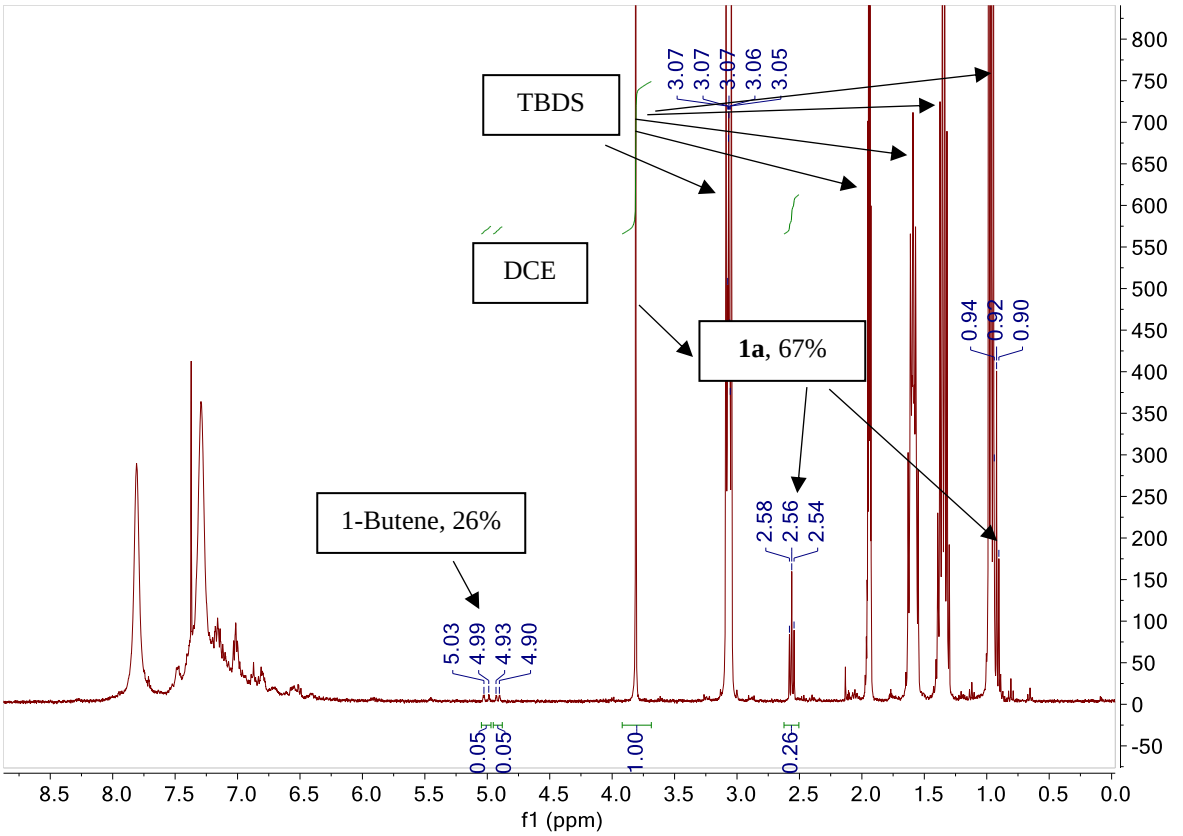


Figure S9. ^{1}H NMR spectra of the reaction of complex 6c and $^{n}Bu_4N^+Ph_4SiF_2^-$.

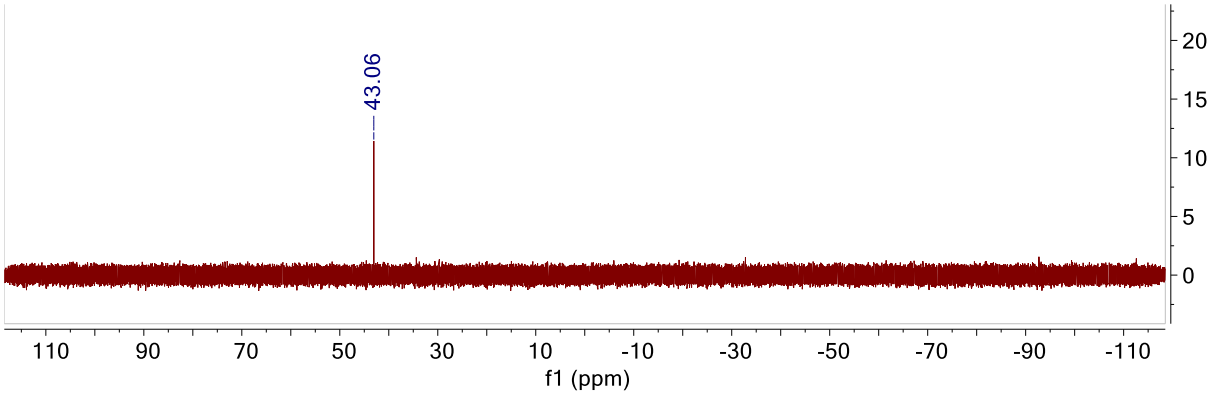


Figure S10. ^{19}F NMR spectra of the reaction of complex 6c and $^{n}Bu_4N^+Ph_4SiF_2^-$.

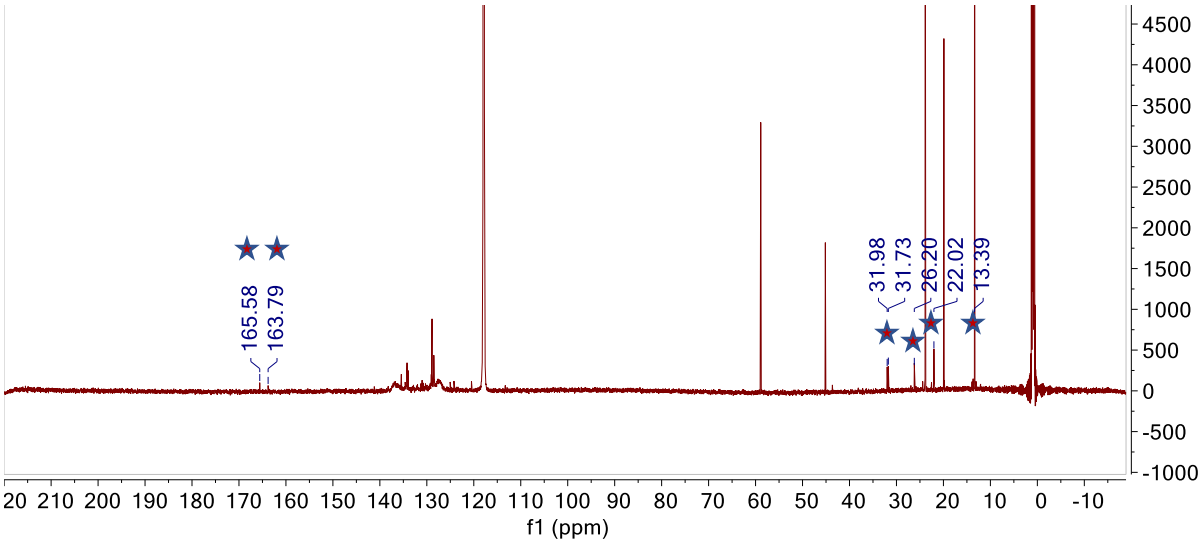


Figure S11. ^{13}C NMR spectra of the reaction of complex 6c and ^{n}Bu$_4$N$^+$Ph$_4$SiF$_2^-$.

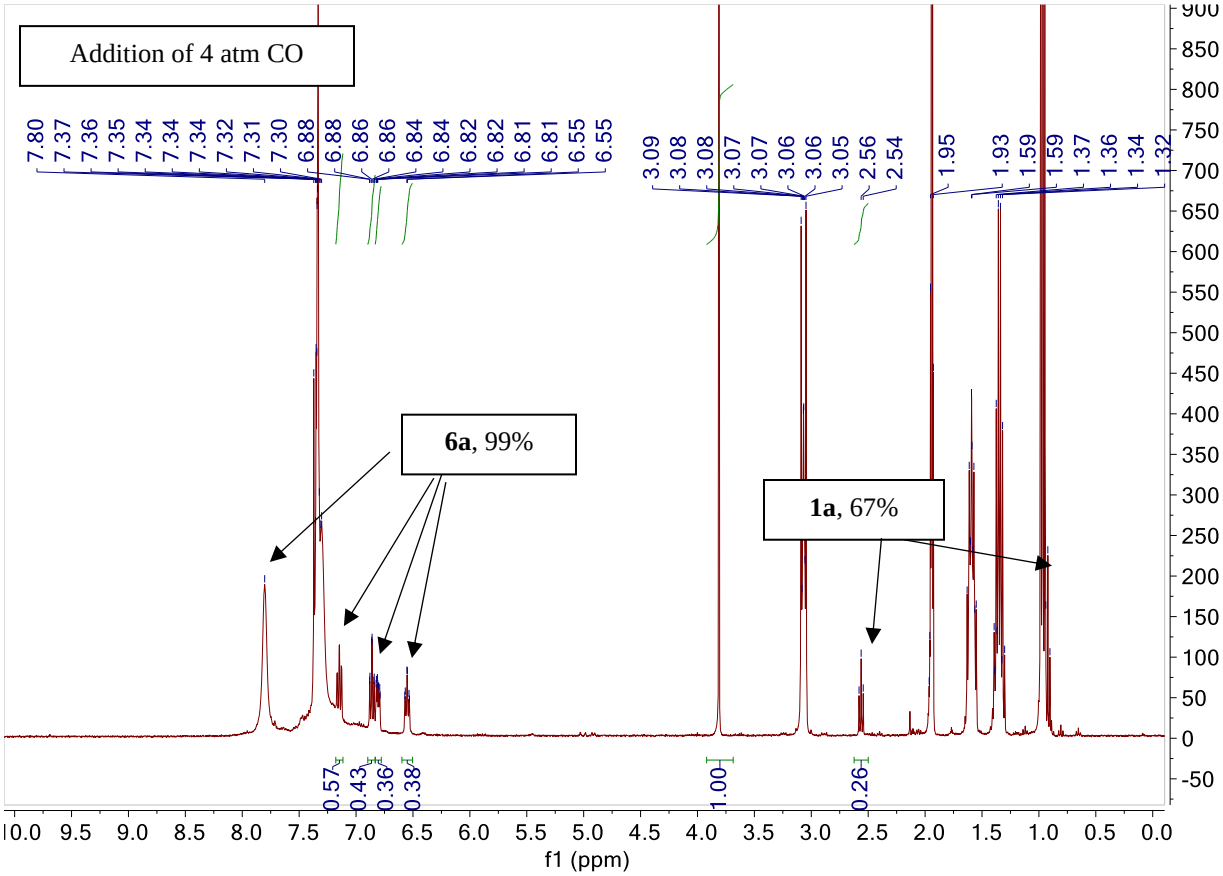


Figure S12. ^{1}H NMR spectra of the reaction of complex 6c and ^{n}Bu$_4$N$^+$Ph$_4$SiF$_2^-$ after the addition of 4 atm CO.

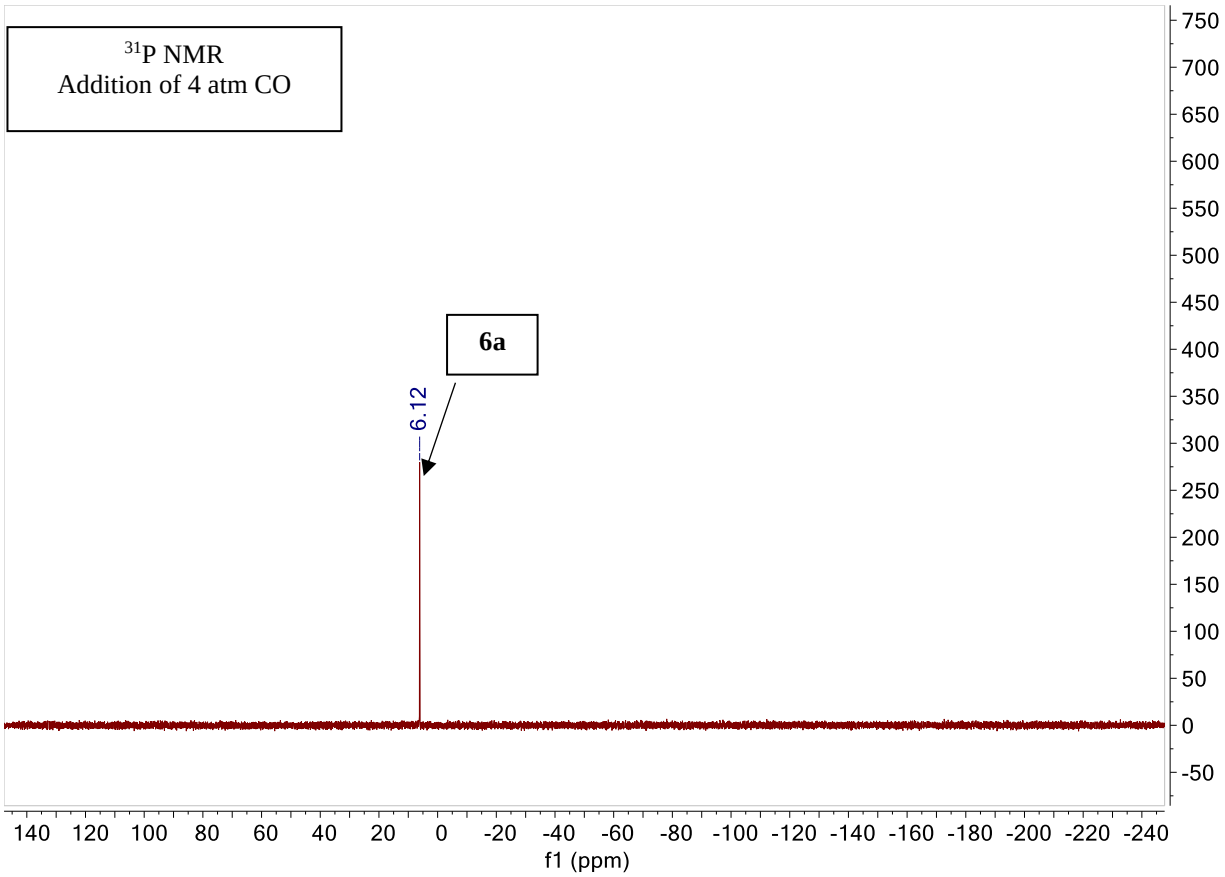
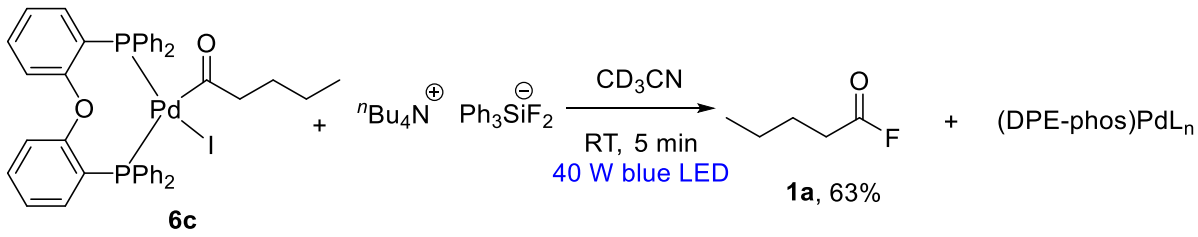
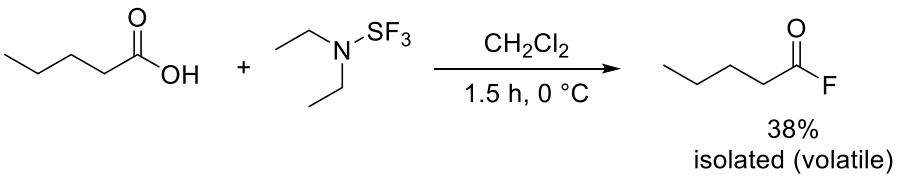


Figure S13. ^{31}P NMR spectra of the reaction of complex 6c and TBDS after the addition of 4 atm CO.



The reaction was conducted using similar procedures as described above, except that the reaction mixture was irradiated with a 40W Blue LED lamp for 5 min before analyzed by NMR spectroscopy. ^{1}H NMR analysis showed the disappearance of complex **6c** and the formation of acyl fluoride **1a** in 63% yield.

Pentanoyl fluoride synthesis

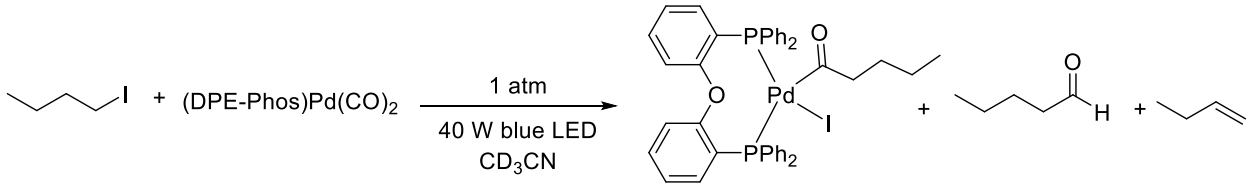


Under nitrogen, valeric acid (2.04 g, 20 mmol) and dry dichloromethane (5 mL) were added to a 50 mL round-bottom flask. The solution was cooled to 0 °C in an ice bath. 1.0 M $(C_2H_5)_2NSF_3$ solution in dichloromethane (22 mL, 22 mmol) was added to the solution dropwise over the course of 2 minutes *via* syringe. The reaction mixture was stirred at 0 °C for 1.5 h. The solvent was removed *via vacuo*. The crude product was purified by vacuum distillation (60 °C, static vacuum at 50 mTorr) to afford pentanoyl fluoride in 38% yield (0.800 g, 7.7 mmol) as a volatile colorless liquid.

^{1}H NMR (500 MHz, CD_3CN) δ 2.56 (t, *J* = 7.4 Hz, 2H), 1.65 – 1.57 (m, 2H), 1.43 – 1.32 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, CD_3CN) δ 164.1 (d, *J* = 358.9 Hz), 31.3 (d, *J* = 49.9 Hz), 25.6 (d, *J* = 2.3 Hz), 21.5, 12.8. ^{19}F NMR (471 MHz, CD_3CN) δ 43.05.

4.4 Photo-induced oxidative addition of *n*-butyl iodide (Figure 3b).

With 1 atm CO



5 min:	69%	trace	trace
15 min:	44%	23%	11%
45 min:	16%	31%	11%

(DPE-Phos)$Pd(CO)_2$, **6a**, was generated *in situ* upon addition of CO to $[(DPE\text{-}Phos)Pd]_2(\mu\text{-}CO)$. In a glovebox, a stock solution of 4-iodotoluene (7.4 mg, 0.04 mmol) in 1 mL of CD_3CN was prepared. 50 μL of this solution was taken and added to a J-Young NMR tube. $[(DPE\text{-}Phos)Pd]_2(\mu\text{-}CO)$ (1.0 mg, 0.0010 mmol) was transferred to the J-Young NMR tube with 0.75 mL CD_3CN. 1,2-Dichloroethane (0.2 mg, 0.002 mmol) was used as an internal standard. The tube was closed, taken out of the glovebox, frozen under liquid nitrogen. The headspace was evacuated, and then 1 atm

of CO were condensed into the tube. (As noted in the general procedures, this was accomplished by condensing 30 mTorr of a CO filled vacuum line (67 mL volume) into the NMR tube (headspace 2.2 mL)). The reaction mixture was irradiated with a 40W Blue LED lamp for 5 min (see the picture of setup in Figure S5B). ^{1}H NMR analysis shows the formation of complex **6c** in 69% yield (calculated based on the internal standard). Continuing the irradiation leads to a decrease of the yield of complex **6c** and increase of aldehyde and alkene products: 15 min, 44% **6c**, 23% pentanal, 11% 1-butene; 45 min, 16% **6c**, 31% pentanal, 11% 1-butene.

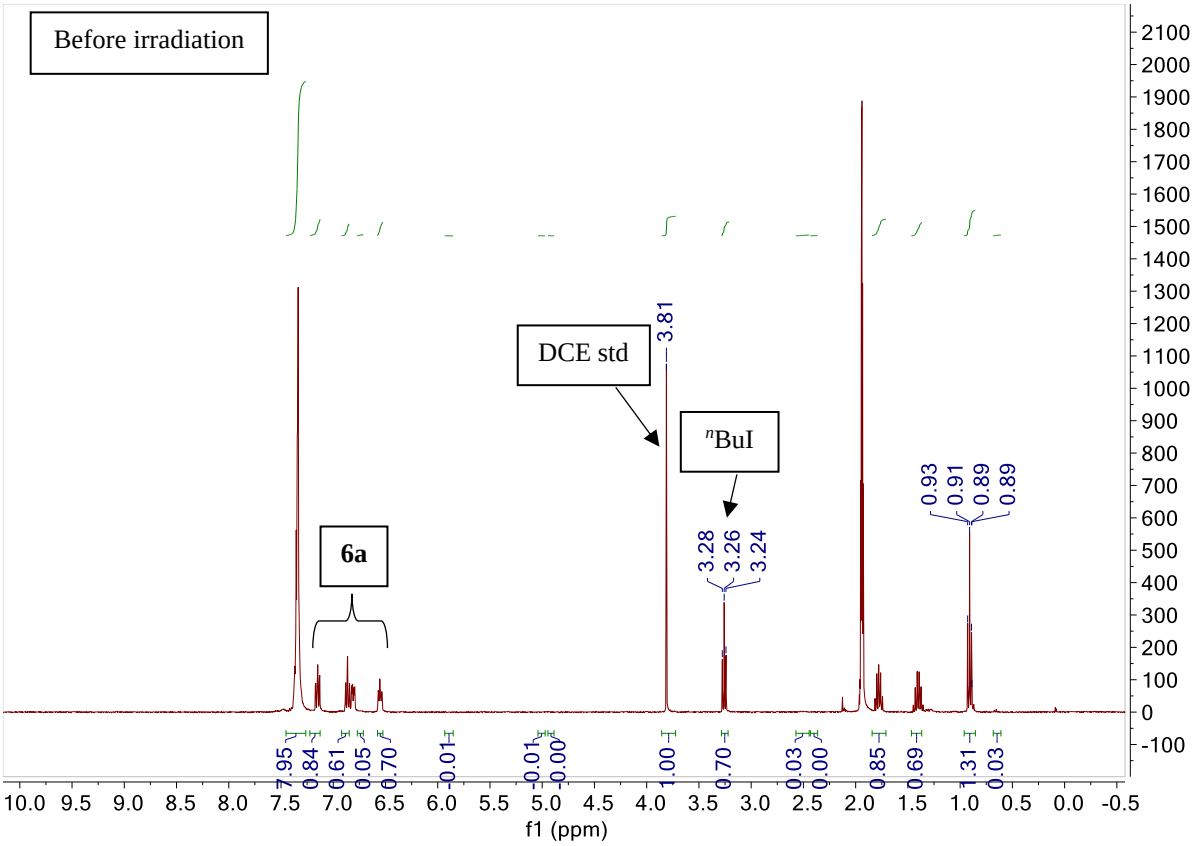


Figure S14. ^{1}H NMR spectra of the reaction of *n*-butyl iodide and complex 6a under 1 atm CO before blue light irradiation.

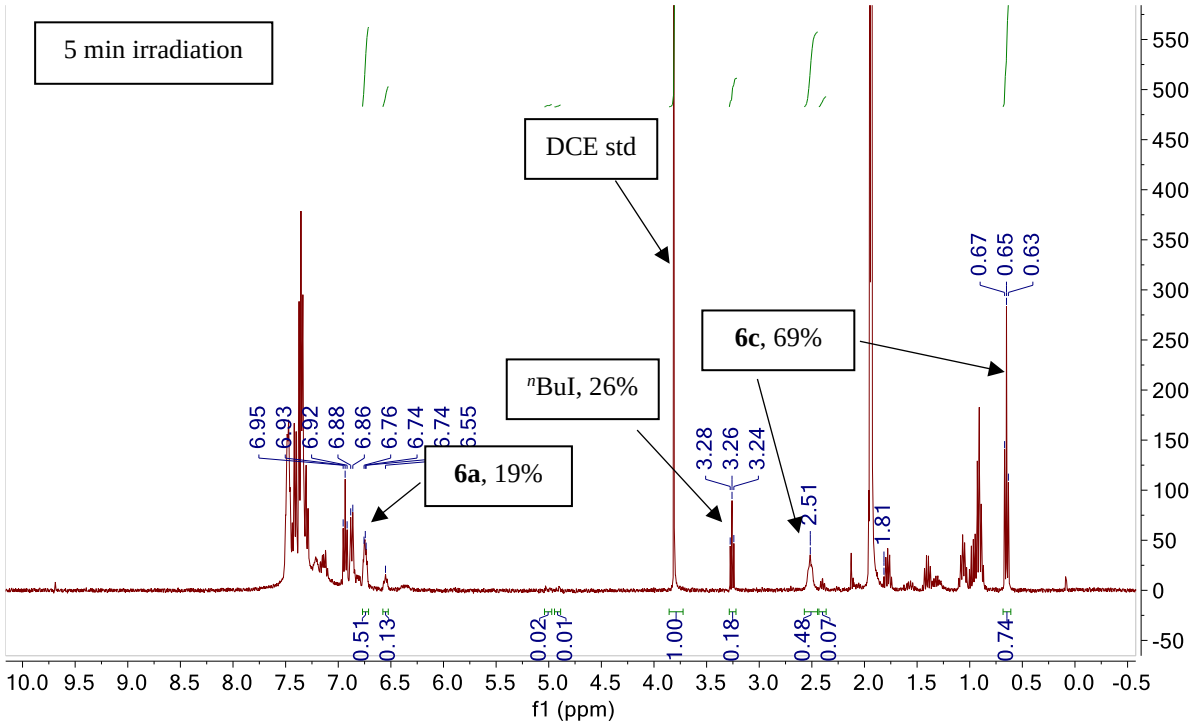


Figure S15. ^{1}H NMR spectra of the reaction of *n*-butyl iodide and complex 6a under 1 atm CO after 5 min of blue light irradiation.

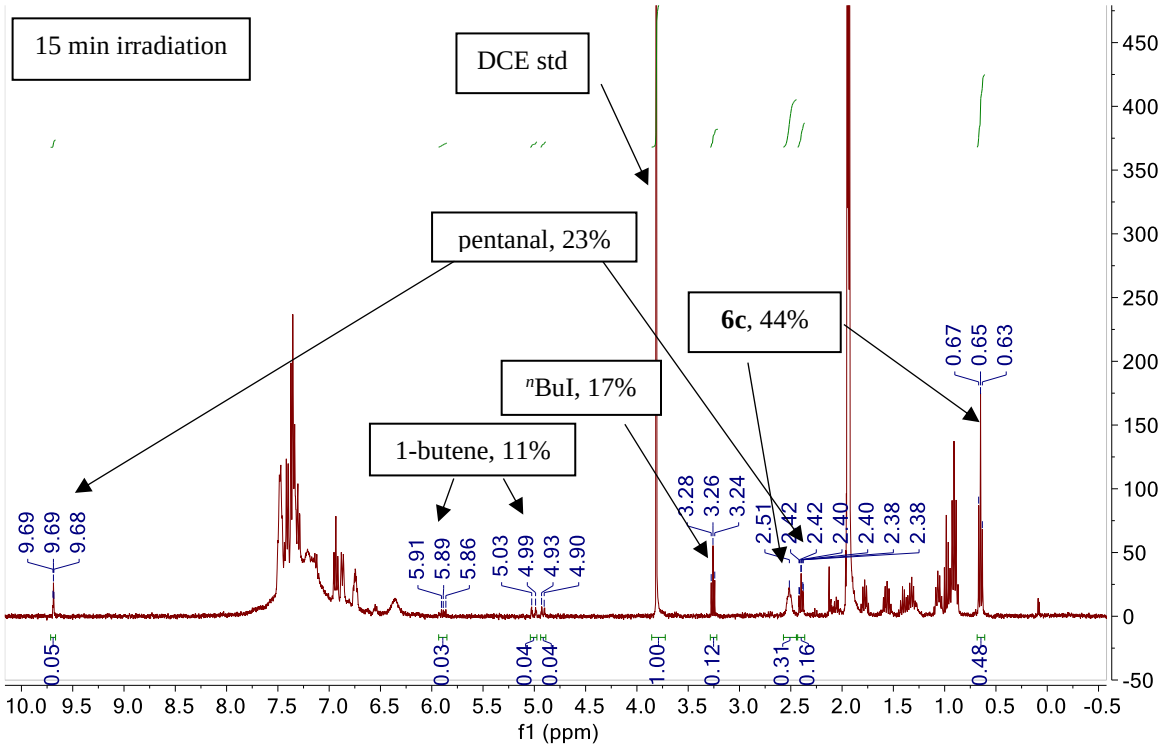


Figure S16. ^{1}H NMR spectra of the reaction of *n*-butyl iodide and complex 6a under 1 atm CO after 15 min of blue light irradiation.

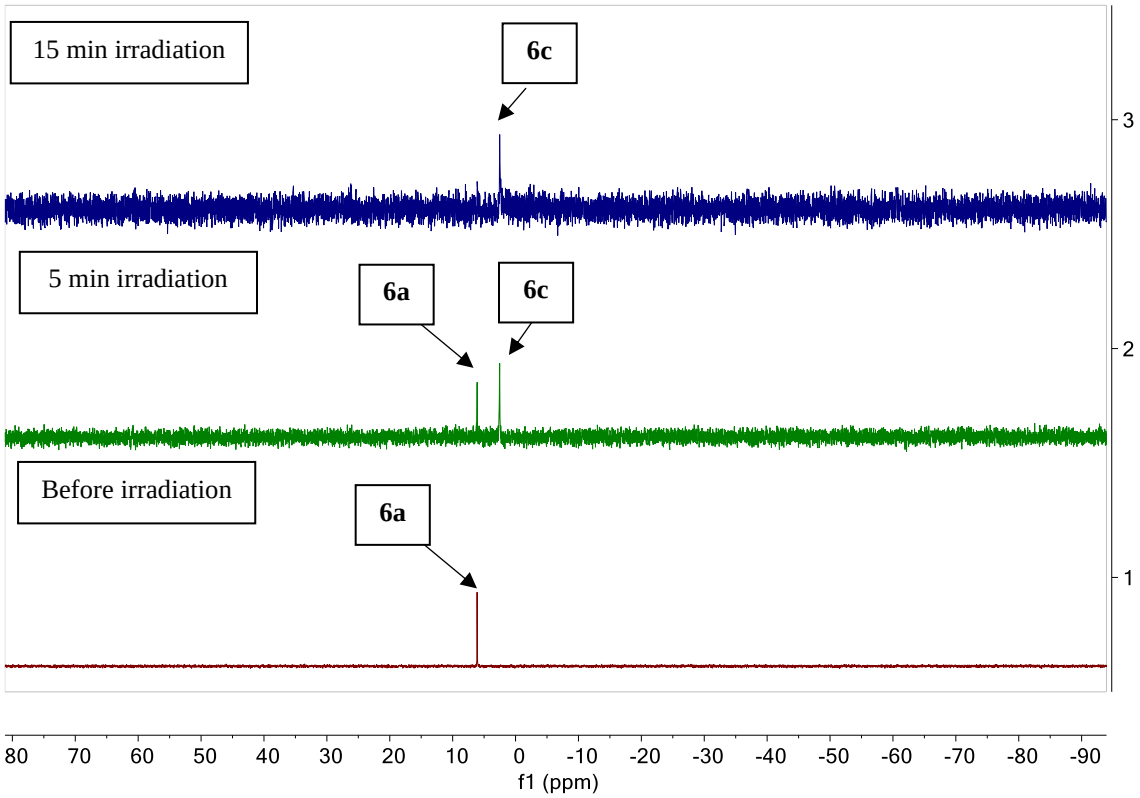
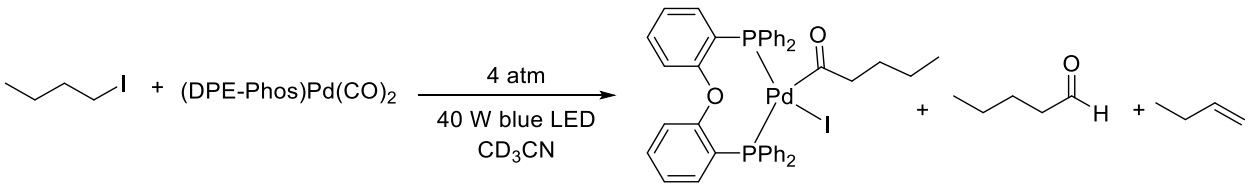


Figure S17. ^{31}P NMR spectra of the reaction of *n*-butyl iodide and complex 6a under 1 atm CO before and after blue light irradiation.

With 4 atm CO



in 25mL vessel (15 min):		48%		
in NMR tube:	5 min:	60%	0%	0%
	15 min:	58%	10%	3%
	45 min:	27%	25%	5%

The reaction was conducted using similar procedures as described above, except with 4 atm of CO (accomplished by condensing 120 mTorr of a CO filled vacuum line (67 mL volume) into the NMR tube (headspace 2.2 mL)). After 5 min of irritation, ^{1}H NMR analysis shows the formation of complex **6c** in 60% yield. Continuing the irradiation for 15 min in total leads to a slight decrease of the yield of complex **6c**, 58%, and the formation of pentanal, 10%, and 1-butene,

3%. Irradiation for 45 min gave 27% **6c**, 25% pentanal, and 5% 1-butene. Performing the same reaction in a 25 mL glass reaction bomb led to the formation of **6c** 48% yield after 15 min.

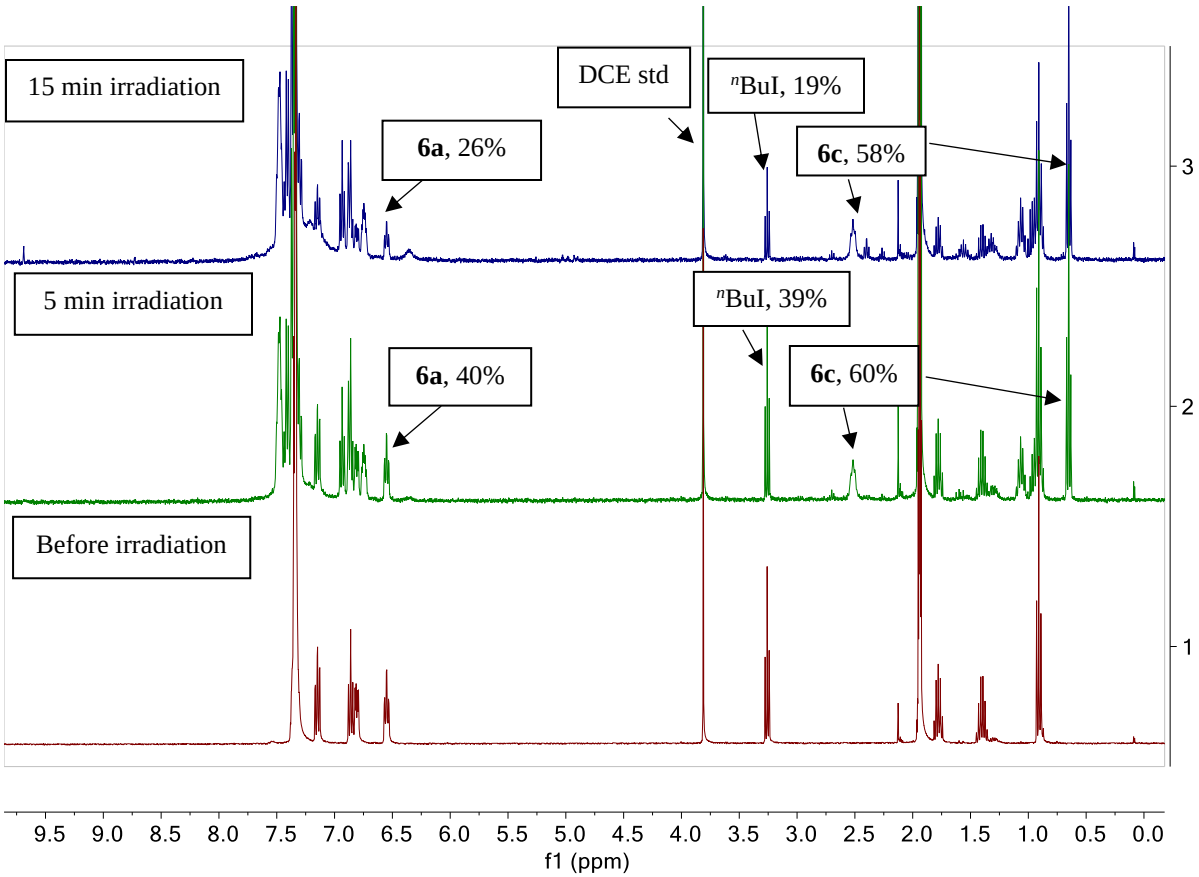
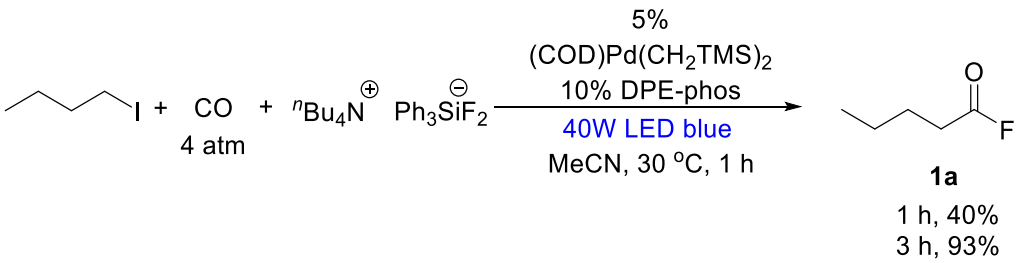


Figure S18. ^{1}H NMR spectra of the reaction of *n*-butyl iodide and complex 6a under 4 atm CO before and after blue light irradiation.

4.5 Study of catalyst resting state

With (COD)Pd(CH$_2$TMS)$_2$/DPE-Phos as the catalyst (Figure 3c)



In a glovebox, tetrabutylammonium difluorotriphenylsilicate (TBDS) (40.5 mg, 0.075 mmol) was dry-transferred into a J-Young NMR tube. 4-iodobutane (9.2 mg, 0.05 mmol), (COD)Pd($CH_2TMS)_2$ (1.0 mg, 0.005 mmol) DPE-Phos (2.7 mg, 0.005 mmol) and 1,2-dichloroethane (1.0 mg, 0.1 mmol) were mixed in a 5 mL vial with 0.75 mL CD_3CN. This suspension was transferred into the J-Young NMR tube. The tube was closed, taken out of the glovebox, frozen under liquid nitrogen. The headspace was evacuated, and then 4 atm of CO were condensed into the tube. (As noted in the general procedures, this was accomplished by condensing 120 mTorr of a CO filled vacuum line (67 mL volume) into the NMR tube (headspace 2.2 mL). The reaction mixture was irradiated with a 40W Blue LED lamp, and the reaction temperature was kept under 30 ºC with two fans (see the picture of setup in Figure S5B). After 1 h, irradiation was stopped, and ^{31}P NMR analysis shows a broad signal at 6.09 ppm corresponding to (DPE-Phos)Pd($CO)_2$ as the only detectable palladium complex, and in the expected ca. 1:1 ratio with uncoordinated DPE-Phos (– 17.20 ppm). The ^{1}H NMR yield of acyl fluoride **1a** was 40% after 1 h, and 93% at 3 h relative to the 1,2-dichloroethane internal standard.

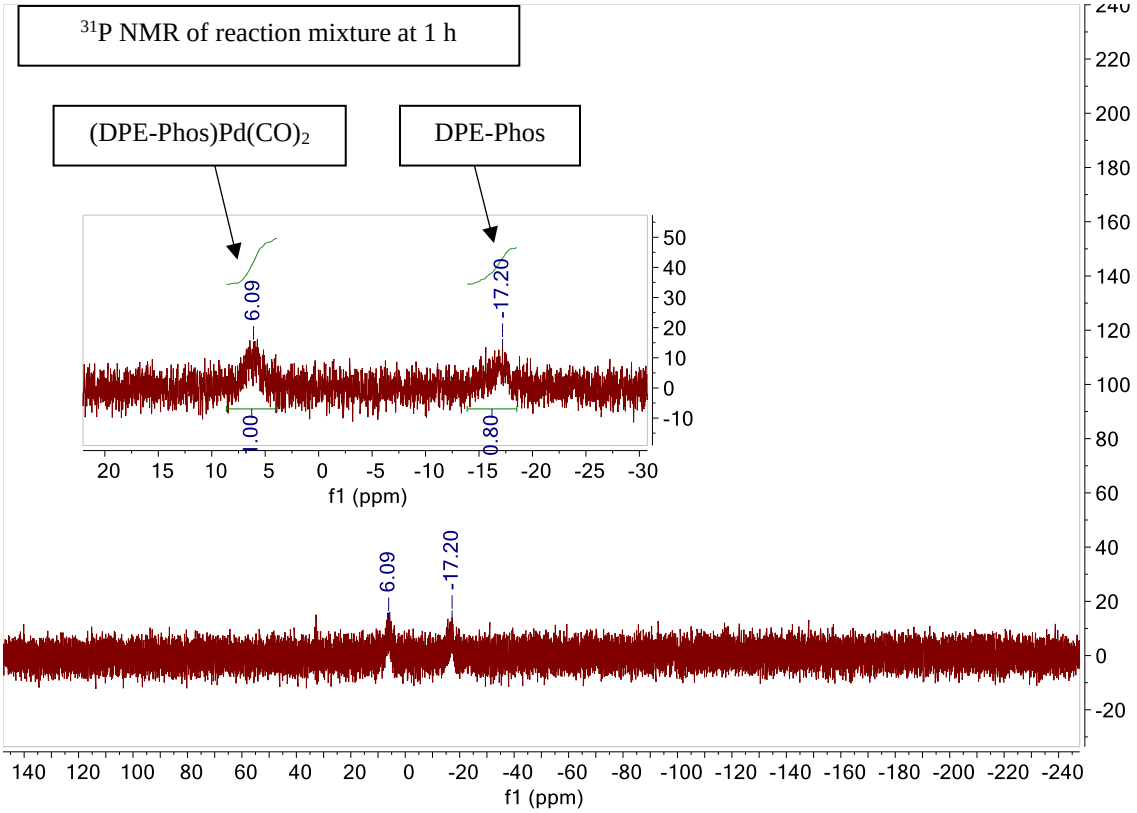
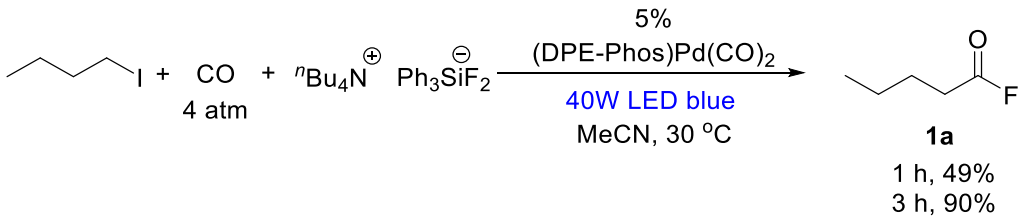


Figure S19. *In situ* ^{31}P NMR of the reaction after 1 hour with (COD)Pd($CH_2TMS)_2$/DPE-Phos as the catalyst.

With (DPE-Phos)Pd(CO)$_2$ *as the catalyst*



The reaction was conducted using similar procedures as described above, except with *in situ* generated (DPE-Phos)Pd(CO)$_2$ as the catalyst. In a glovebox, tetrabutylammonium difluorotriphenylsilicate (TBDS) (40.5 mg, 0.075 mmol) was dry-transferred into a J-Young NMR tube. 4-iodobutane (9.2 mg, 0.05 mmol), [(DPE-Phos)Pd]$_2$(μ-CO) (1.6 mg, 0.0013 mmol) and 1,2-dichloroethane (1.0 mg, 0.1 mmol) were mixed in a 5 mL vial with 0.75 mL CD_3CN. This suspension was transferred into the J-Young NMR tube. The tube was closed, taken out of the glovebox, frozen under liquid nitrogen. The headspace was evacuated, and then 4 atm of CO were condensed into the tube. After 1 h, irradiation was stopped, and ^{31}P NMR analysis shows only the presence of (DPE-Phos)Pd(CO)$_2$ (99% yield, calculated *via* ^{1}H NMR analysis relative to the 1,2-dichloroethane internal standard). The yield of acyl fluoride **1a** was 49% at 1 h and 90% at 3 h.

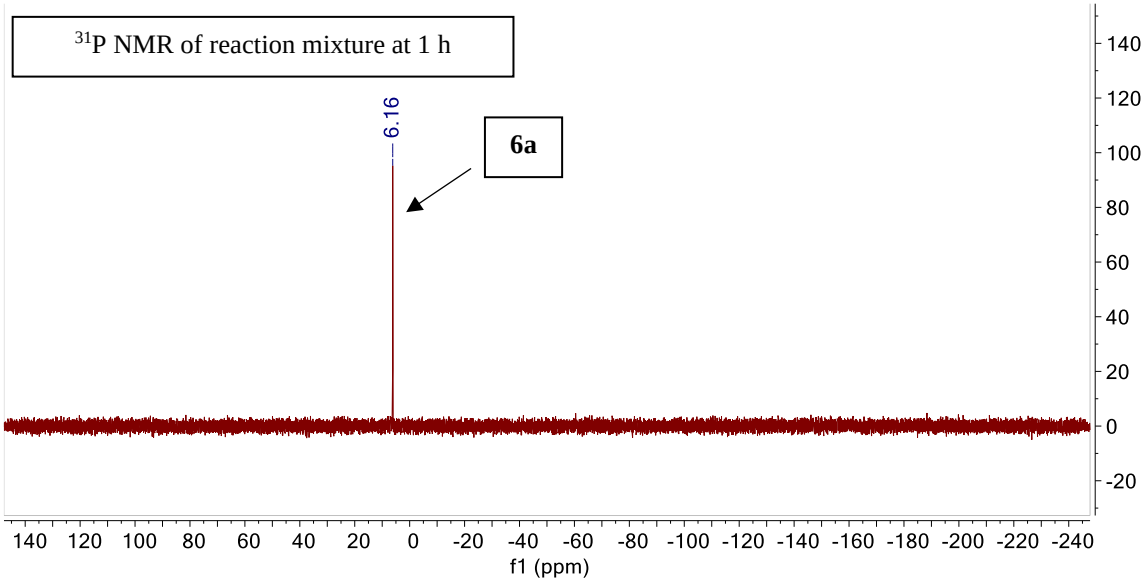


Figure S20. ^{31}P NMR of the reaction mixture at 1 hour.

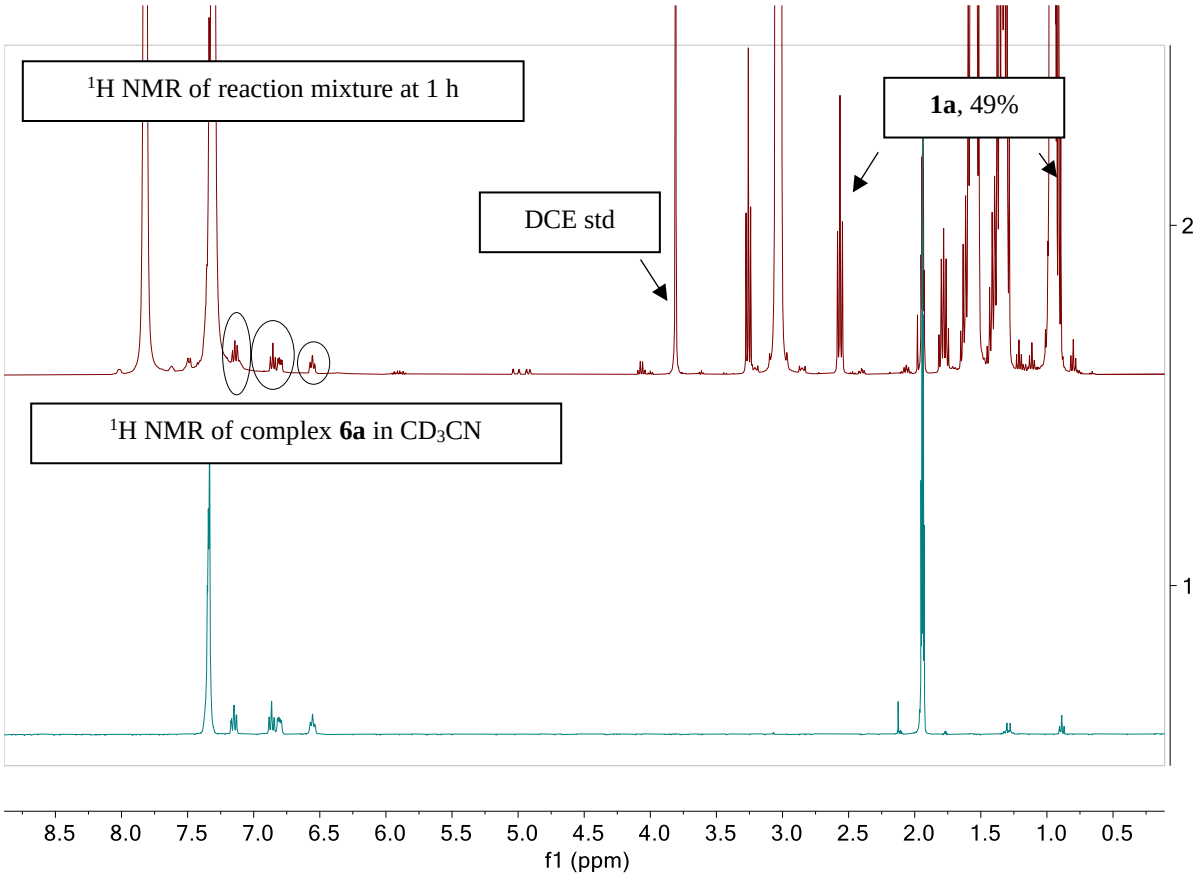
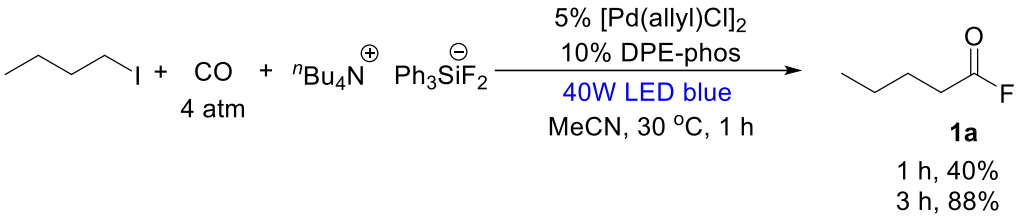


Figure S21. ^{1}H NMR of the reaction mixture using complex 6a as the catalyst.

With [Pd(allyl)Cl]$_2$/DPE-Phos as the catalyst



The reaction was conducted using similar procedures as described above, except with [Pd(allyl)Cl]$_2$ (200 uL of 6.5 mM solution in CD_3CN, 0.0013 mmol) and DPE-Phos (2.7 mg, 0.005 mmol) as the catalyst. After 1 h, irradiation was stopped, and ^{31}P NMR analysis shows the formation of complex **6a**, along with other unidentified signals. The yields of acyl fluoride **1a**, 40% at 1 hour and 88% at 3 hours.

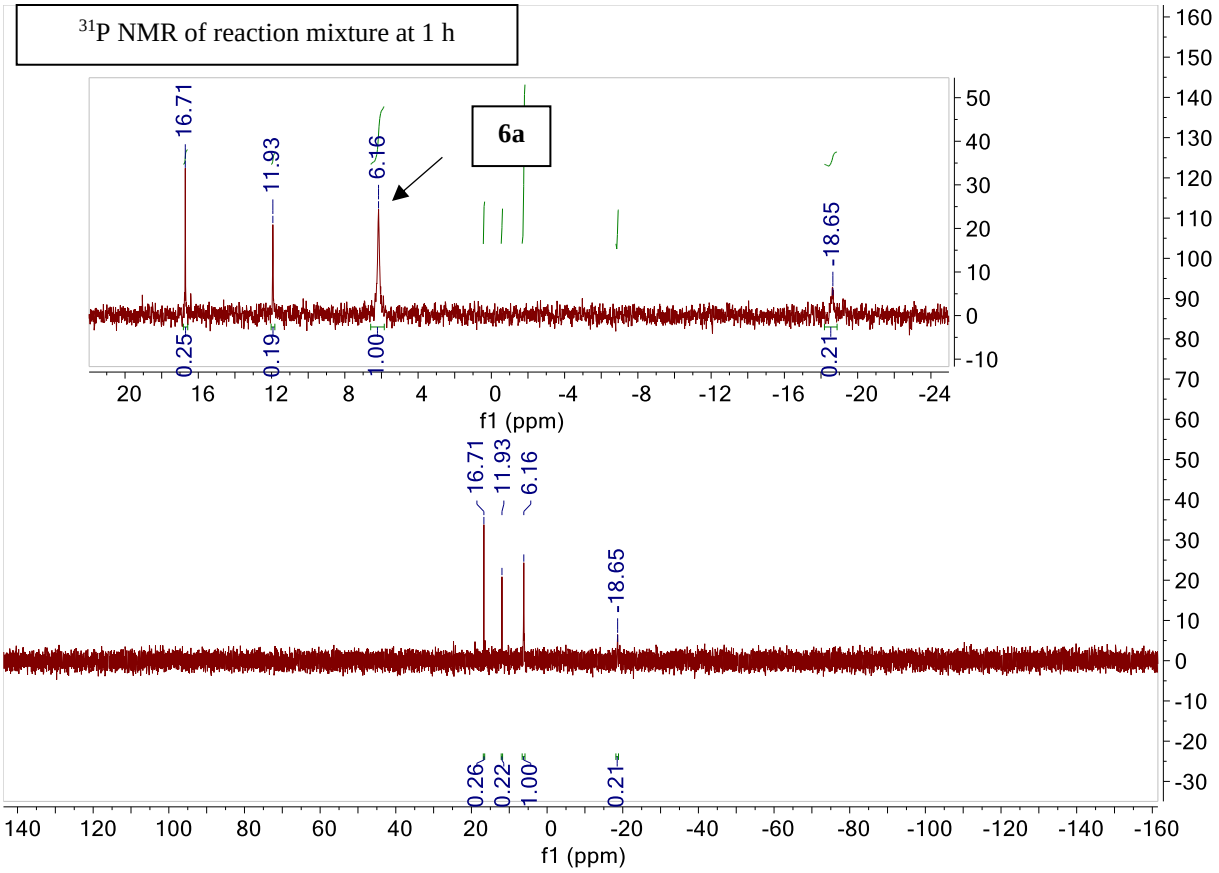
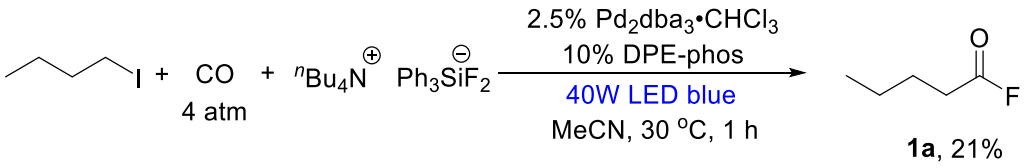


Figure S22. ^{31}P NMR of the reaction mixture using [Pd(allyl)Cl]$_2$/DPE-Phos as the catalyst.

With Pd_2dba_3•$CHCl_3$/DPE-Phos as the catalyst



The reaction was conducted using similar procedures as described above, except with Pd_2dba_3•$CHCl_3$ (1.3 mg, 0.0013 mmol) and DPE-Phos (2.7 mg, 0.005 mmol) as the catalyst. ^{31}P NMR analysis after 1 h shows the formation of a broad peak at 6.42 ppm, which may correspond to complex **6a** undergoing exchange with other ligands, such as dba. The yield of acyl fluoride **1a,** 21%, was calculated *via* ^{1}H NMR analysis relative to the 1,2-dichloroethane internal standard. After 3 h, many other signals were observed in ^{31}P NMR, suggesting the decomposition of the catalyst. The yield of acyl fluoride **1a** was 45% at 3 h, and 75% at 15 h.

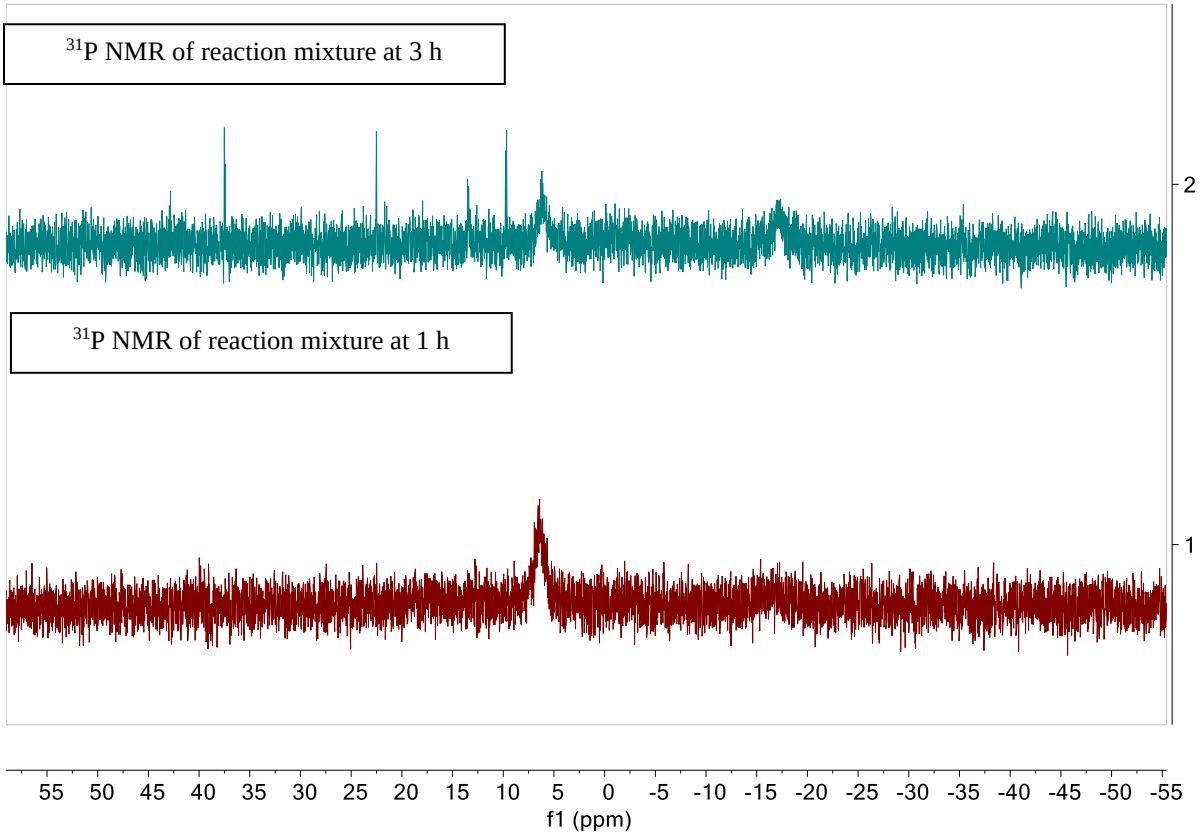
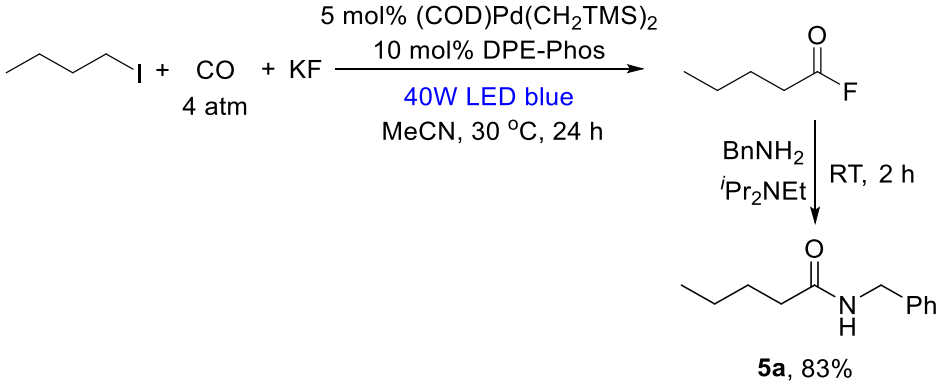


Figure S23. ^{31}P NMR of the reaction mixture using Pd_2dba_3•$CHCl_3$/DPE-Phos as the catalyst.

5. Catalytic carbonylative generation of acyl fluorides (Figure 4 and 5a)

5.1 Synthesis of alkyl acyl fluorides

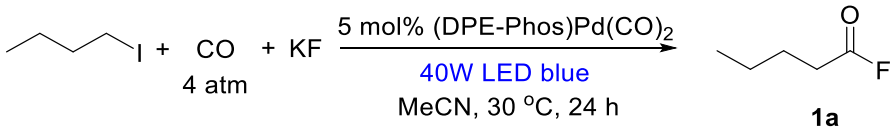


5a, 83%

In a glovebox, *n*-butyl iodide (36.8 mg, 0.20 mmol), (COD)Pd($CH_2TMS)_2$ (3.9 mg, 0.010 mmol), DPE-Phos (10.8 mg, 0.020 mmol) and benzyl benzoate standard (4.2 mg, 0.020 mmol) were dissolved in 4 mL of CH_3CN. The mixture was transferred into a thick-walled 25 mL glass reaction vessel equipped with a magnetic stir bar and a Teflon cap. A suspension of potassium fluoride (23.2 mg, 0.40 mmol) was prepared in 2 mL CH_3CN and transferred to the vessel. The vessel was closed, taken out of the glovebox and attached to a CO line. Before opening the vessel, the connecting tubing was evacuated and backfilled with carbon monoxide three times, and finally, the vessel was opened and pressurized with 4 atm carbon monoxide (on top of 1 atm of nitrogen). The vessel was closed and clamped on top of a stirring plate, and the solution was irradiated using a 40W Blue LED lamp. Fans were used to keep the temperature below 30 ºC (see the picture of setup in Figure S5A). After 24 hours, the vessel was taken out of the irradiation system and attached to a Schlenk line. The mixture was frozen by liquid nitrogen, and the excess CO was removed by opening the cap to vacuum. The vessel was brought into the glovebox. Benzylamine (42.9 mg, 0.40 mmol) and EtN^iPr_2 base (51.7 mg, 0.40 mmol) were added. The mixture was allowed to stir at room temperature for 2 hours. The product was isolated by column chromatography: Silica gel, gradient hexane (with 2% NEt_3)/ethyl acetate 20% to 40%, affording pure amide **5a** as a pale-yellow solid in 83% yield (31.9 mg, 0.17 mmol).

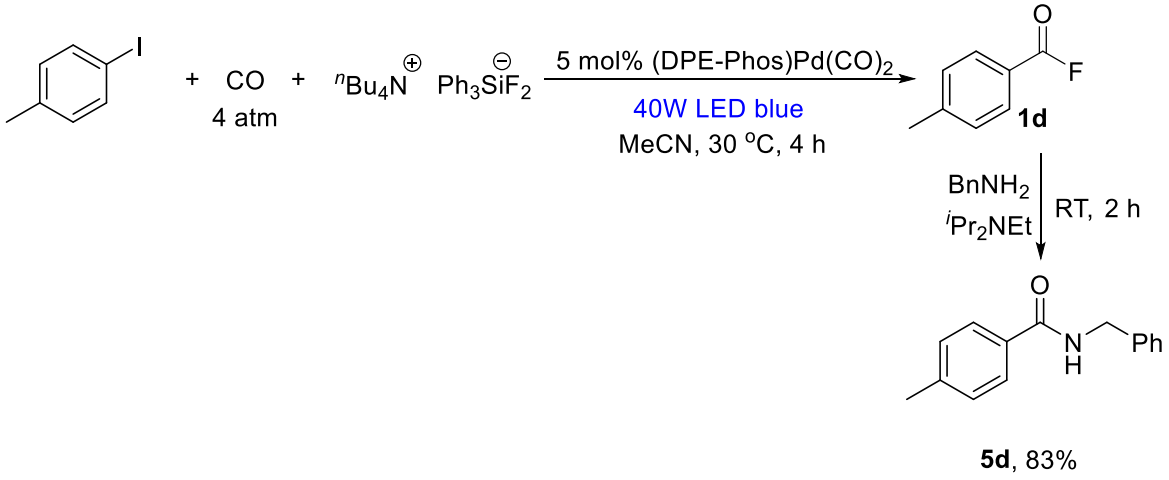
Similar procedures were used for other alkyl acyl fluorides formation except the following modifications: **1v**, **1x**, **1z**, **1bb-ee**, **1ii**, **1ll-tt**, **1vv-iii**: 10% palladium catalyst; **1u**, **1y**, **1z**, **1gg**: (DPE-Phos)Pd($CO)_2$ as catalyst; **1ll-pp**, **1ss**, **1aaa**, **1ddd**, **1fff-hhh**: 48 h. **4f**, **4k**, **4l** 10% (DPE-Phos)Pd($CO)_2$; **4g. 4h, 4i, 4j**: 10% (COD)Pd($CH_2TMS)_2$/15% DPE-Phos, 0.20 mmol of alkyl bromide substrate and 0.30 mmol of tetrabutylammonium difluorotriphenylsilicate (TBDS) as fluoride the source.

5.2 Generation of alkyl acyl fluorides for *in situ* characterization



Catalyst (DPE-Phos)Pd(CO)$_2$ was generated in situ upon addition of carbon monoxide to [(DPE-Phos)Pd]$_2$(μ-CO). In a glovebox, *n*-butyl iodide (18.4 mg, 0.10 mmol) and [(DPE-Phos)Pd]$_2$(μ-CO) (3.3 mg, 0.0025 mmol) were dissolved in 2 mL of CD_3CN. The mixture was transferred into a thick-walled 25 mL glass reaction vessel equipped with a magnetic stir bar and a Teflon cap. A suspension of potassium fluoride (11.6 mg, 0.20 mmol) was prepared in 1 mL CH_3CN and transferred to the vessel. The vessel was closed, taken out of the glovebox and attached to a CO line. Before opening the vessel, the connecting tubing was evacuated and backfilled with carbon monoxide three times, and finally, the vessel was opened and pressurized with 4 atm carbon monoxide (on top of 1 atm of nitrogen). The vessel was closed and clamped on top of a stirring plate, and the solution was irradiated using a 40W Blue LED lamp. Fans were used to keep the temperature below 30 ºC (see the picture of setup in Figure S5A). After 24 hours, the vessel was taken out of the irradiation system and attached to a Schlenk line. The mixture was frozen by liquid nitrogen, and the excess CO was removed by opening the cap to vacuum. The vessel was brought into the glovebox. An aliquot was taken, and the acyl fluoride product was characterized *in situ* by ^{1}H, ^{19}F and ^{13}C NMR analysis.

5.3 Synthesis of aryl acyl fluorides



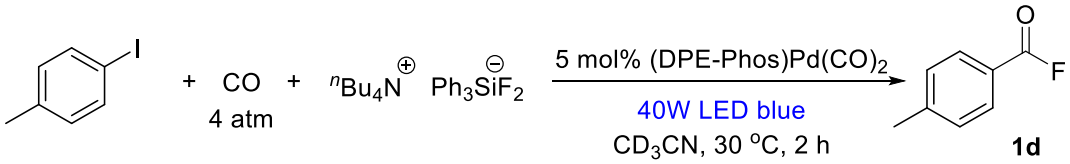
5d, 83%

Catalyst (DPE-Phos)Pd(CO)$_2$ was generated in situ upon addition of carbon monoxide to [(DPE-Phos)Pd]$_2$(μ-CO). In a glovebox, tetrabutylammonium difluorotriphenylsilicate (TBDS) (162 mg, 0.30 mmol) was dry-transferred into a thick-walled 25 mL glass reaction vessel equipped

with a magnetic stir bar and a Teflon cap. 4-iodotoluene (43.6 mg, 0.20 mmol), [(DPE-Phos)Pd]$_2$(μ-CO) (13.2 mg, 0.010 mmol) and 1,2-dichloroethane (1.0 mg, 0.10 mmol) internal standard were mixed in a 5 mL vial with 3.2 mL CH_3CN. This suspension was transferred to the vessel. The vessel was closed, taken out of the glovebox and attached to a CO line. Before opening the vessel, the connecting tubing was evacuated and backfilled with carbon monoxide three times, and finally, the vessel was opened and pressurized with 4 atm carbon monoxide (on top of 1 atm of nitrogen). The vessel was closed and clamped on top of a stirring plate, and the solution was irradiated using a 40W Blue LED lamp. Fans were used to keep the temperature below 30 ºC (see the picture of setup in Figure S5A). After 4 hours, the vessel was taken out of the irradiation system and attached to a Schlenk line. The excess CO was removed by opening the cap to under N_2 flow. Benzylamine (0.05 mL, 0.40 mmol) and EtN^iPr_2 base (0.07 mL, 0.40 mmol) were quickly added *via* syringes under N_2 flow. The mixture was stirred at room temperature for 2 hours. The product was isolated by column chromatography: Silica gel, gradient hexane/ethyl acetate 10% to 40%, affording pure amide **5d** as a pale-yellow solid in 83% yield (37.4 mg, 0.17 mmol).

Similar procedures were used for other aryl acyl fluorides formation except for the following modifications: **1f**, **1i, 1k, 1l**: 8 h; **1m-s**: 24 h.**1e** and **1j**: 1 mmol scale. **1k** and **1m-q**: 10% (DPE-Phos)Pd(CO)$_2$.

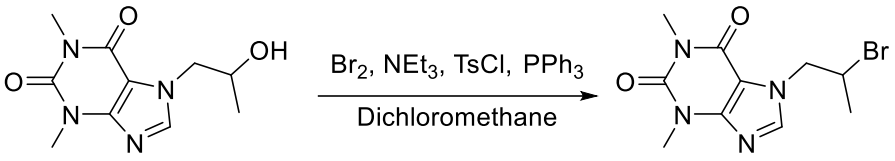
5.4 Generation of aryl acyl fluorides for *in situ* characterization



Catalyst (DPE-Phos)Pd(CO)$_2$ was generated in situ upon addition of carbon monoxide to [(DPE-Phos)Pd]$_2$(μ-CO). In a glovebox, tetrabutylammonium difluorotriphenylsilicate (TBDS) (40.5 mg, 0.075 mmol) was dry-transferred into a J-Young NMR tube. 4-iodotoluene (11.0 mg, 0.05 mmol) and [(DPE-Phos)Pd]$_2$(μ-CO) (1.6 mg, 0.0012 mmol) were mixed in a 5 mL vial with 0.75 mL CD_3CN. This suspension was transferred into the J-Young NMR tube. The tube was closed, taken out of the glovebox, frozen under liquid nitrogen. The headspace was evacuated, and then 4 atm of CO were condensed into the tube. (As noted in the general procedures, this was

accomplished by condensing 120 mTorr of a CO filled vacuum line (67 mL volume) into the NMR tube (headspace 2.2 mL). The reaction mixture was irradiated with a 40W Blue LED lamp, and the reaction temperature was kept under 30 ºC with two fans (see the picture of setup in Figure S5B). After 2 hours, irradiation was stopped, and the acyl fluoride product was characterized *in situ* by ^{1}H, ^{19}F and ^{13}C NMR analysis.

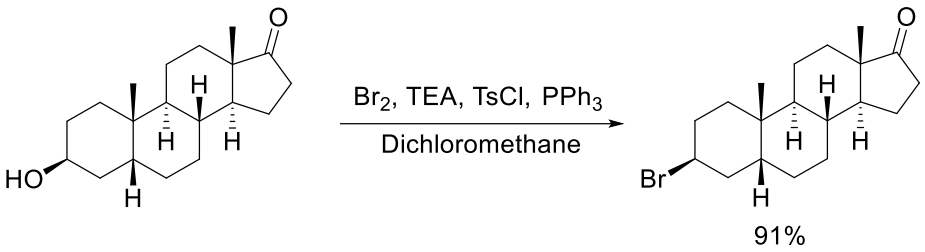
6. Synthesis of alkyl bromides



63%

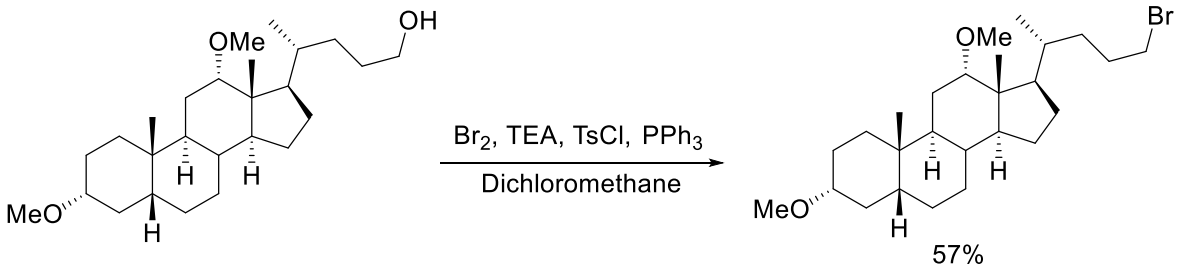
The following procedure was adapted from the literature.[2] Triphenylphosphine (525 mg, 2.0 mmol) and dry dichloromethane (25 mL) were added to a 100 mL round-bottom flask. The solution was cooled to 0 °C, and bromine (0.08 mL, 1.5 mmol) was added dropwise to the solution. Triethylamine (0.21 mL, 1.5 mmol) and *p*-toluenesulfonyl chloride (42 mg, 0.2 mmol) were added, and the reaction was stirred for 10 minutes at 0 °C. A solution of 238 mg (1.0 mmol) of proxyphylline in dichloromethane (5 mL) was added dropwise over the course of 2 min to the mixture. The reaction mixture was allowed to warm up to room temperature and stirred overnight. The reaction was quenched with water, and the aqueous layer was extracted with ethyl acetate (30 mLx3). The combined organic layers were washed with water (30 mL) and brine (30 mL x 2), and then was dried over Na_2SO_4 followed by filtration. The solvent was removed *in vacuo* to give the crude product. The residue was purified by reverse-phase chromatography on C18 silica with acetonitrile/water (10-100%). The fractions were condensed and dried with lyophilizer, affording the product in 63% yield (190 g, 0.63 mmol) as a white low melting point solid.

7-(2-bromopropyl)-1,3-dimethyl-3,7-dihydro-1H-purine-2,6-dione (S1). ^{1}H NMR (800 MHz, $CDCl_3$) δ 7.66 (s, 1H), 4.69 (dd, *J* = 14.3, 3.8 Hz, 1H), 4.51 (dqd, *J* = 9.2, 6.7, 3.8 Hz, 1H), 4.30 (dd, *J* = 14.3, 9.2 Hz, 1H), 3.60 (s, 3H), 3.40 (s, 3H), 1.79 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (201 MHz, $CDCl_3$) δ 155.3, 151.6, 149.2, 141.9, 132.1, 132.1, 128.5, 128.5, 106.6, 55.0, 47.8, 29.9, 28.0, 23.1. HRMS: calculated for $C_{10}H_{13}BrN_4O_2Na^+$ ($M+Na^+$): 323.0114, found: 323.0105.



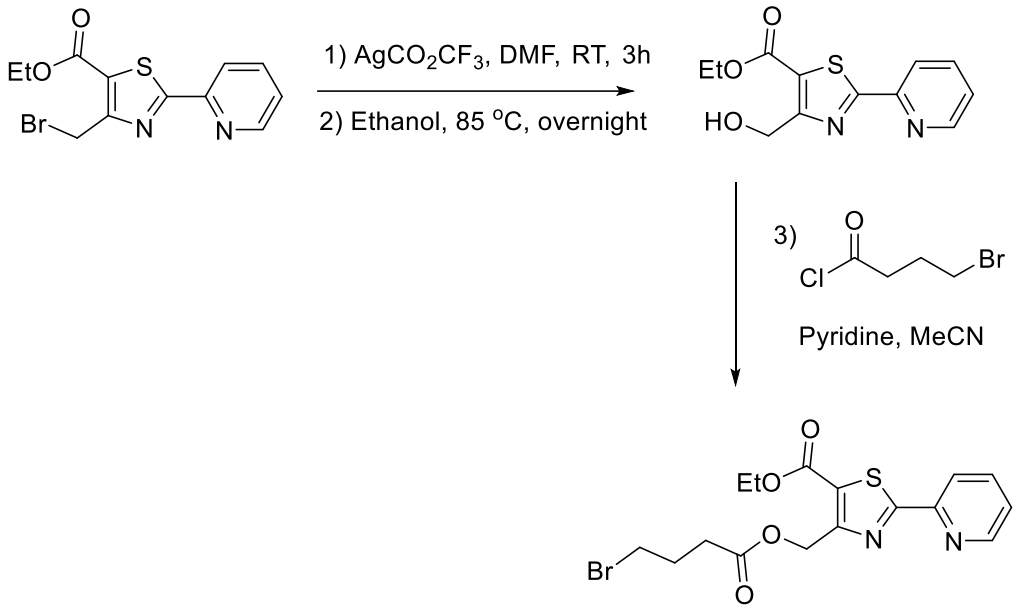
The reaction was conducted using similar procedures as described above, except with *trans*-androsterone (330 mg, 1.1 mmol), triphenylphosphine (578 mg, 2.2 mmol), bromine (0.09 mL, 1.6 mmol), triethylamine (0.23 mL, 1.6 mmol), *p*-toluenesulfonyl chloride (42 mg, 0.2 mmol) and dry dichloromethane (33 mL). The crude product was purified by flash chromatography on silica gel (230-400 mesh) with ethyl acetate/hexanes (5-10% gradient), affording the product in 91% yield (0.35 g, 1.0 mmol) as a white solid.

(3S,5R,8R,9S,10S,13S,14S)-3-bromo-10,13-dimethylhexadecahydro-17H-cyclopenta[a]phenanthren-17-one. NMR spectral data are the same as that previously reported in the literature.[1] ^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.72 (t, *J* = 2.8 Hz, 1H), 2.43 (ddd, *J* = 19.1, 8.9, 1.1 Hz, 1H), 2.07 (dt, *J* = 19.2, 9.0 Hz, 1H), 1.94 (qt, *J* = 8.3, 3.8 Hz, 3H), 1.85 – 1.65 (m, 6H), 1.61 – 1.40 (m, 4H), 1.35 – 1.18 (m, 5H), 1.13 – 0.98 (m, 1H), 0.94 – 0.87 (m, 1H), 0.85 (s, 3H), 0.81 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.3, 55.6, 54.0, 51.4, 47.8, 40.2, 37.2, 36.4, 35.8, 35.0, 32.9, 31.5, 30.9, 30.6, 27.6, 21.7, 20.1, 13.8, 12.3.



The reaction was conducted using similar procedures as described above, except with di-methoxy-ethyl-deoxycholate (150 mg, 0.38 mmol), triphenylphosphine (200 mg, 0.76 mmol), bromine (0.03 mL, 0.6 mmol), triethylamine (0.08 mL, 0.6 mmol), *p*-toluenesulfonyl chloride (16 mg, 0.08 mmol) and dry dichloromethane (11 mL). The crude product was purified by flash chromatography on silica gel (230-400 mesh) with ethyl acetate/hexanes (5-10% gradient), affording the product in 57% yield (0.10 g, 0.21 mmol) as a pale-yellow oil.

(3R,5R,9S,10S,12S,13R,14S,17R)-17-((R)-5-bromopentan-2-yl)-3,12-dimethoxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthrene. NMR spectral data are the same as that previously reported in the literature.[1] ^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.44 – 3.34 (m, 3H), 3.33 (s, 3H), 3.24 (s, 3H), 3.14 (tt, *J* = 10.8, 4.4 Hz, 1H), 1.99 – 1.64 (m, 10H), 1.64 – 1.44 (m, 4H), 1.36 (t, *J* = 11.7 Hz, 4H), 1.29 – 0.93 (m, 8H), 0.91 (t, *J* = 3.3 Hz, 6H), 0.66 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.2, 80.5, 55.6, 55.5, 48.8, 46.6, 46.33, 42.1, 36.0, 35.3, 35.0, 34.6, 34.5, 34.44, 33.5, 32.6, 29.7, 27.5, 27.4, 26.8, 26.1, 23.7, 23.3, 21.9, 17.7, 12.7.

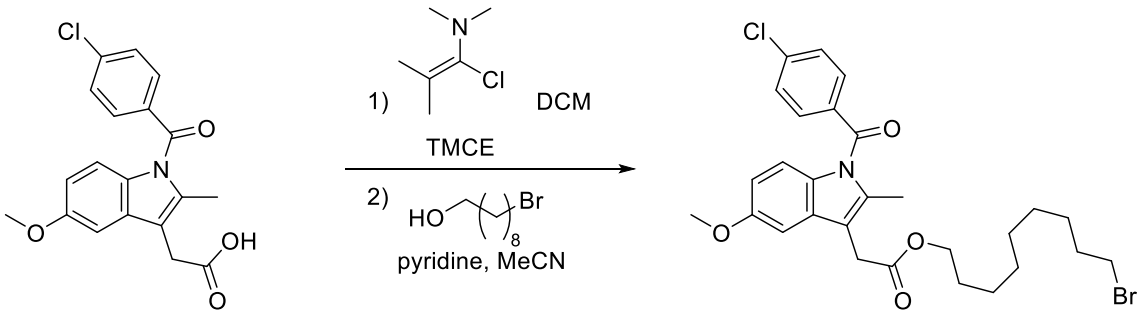


A modified procedure was employed. Ethyl 4-(bromomethyl)-2-(pyridin-2-yl)thiazole-5-carboxylate (1 equiv., 2 mmol, 654 mg) was dissolved in 7 ml dry DMF in the N_2 glovebox. Silver trifluoroacetate solid (1.5 equiv, 3 mmol, 663 mg) was added to the solution. A green precipitation instantly formed. The reaction mixture was stirred at room temperature for 3 h, then brought outside the glovebox, quench with 5 ml distilled water, and extracted with 15 ml diethyl ether. The organic phase was washed with distilled water (2 x 5 ml) then dried with sodium sulfate, filtered, and concentrated in vacuo. The yellow solid was collected and dissolved in 6 ml ethanol in a clean, dry 50 ml round bottom flask. The reaction mixture was refluxed at 85°C for 16 h and then concentrated in vacuo. The light-yellow solid was collected and directly used in the next step. Ethyl 4-(hydroxymethyl)-2-(pyridin-2-yl)thiazole-5-carboxylate was transferred to a clean and dry 20 ml vial and 5 ml MeCN was added. 4-bromobutanoyl chloride (1.2 equiv., 2.4 mmol, 278 μl)

and pyridine (1.2 equiv., 2.4 mmol, 202 μl) were added to the solution. The reaction mixture was stirred for 1 h then concentrated in vacuo. The crude residue was purified by flash chromatography on silica gel (230-400 mesh) with ethyl acetate/hexane (10 – 70% gradient), affording the product in 43% yield (358 mg, 0.86 mmol) as a white solid.

Ethyl 4-(hydroxymethyl)-2-(pyridin-2-yl)thiazole-5-carboxylate (S2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (ddd, *J* = 4.8, 1.8, 1.0 Hz, 1H), 8.22 (ddd, *J* = 7.9, 1.1, 1.1 Hz, 1H), 7.84 (ddd, *J* = 7.7, 7.7, 1.7 Hz, 1H), 7.39 (ddd, *J* = 7.6, 4.8, 1.2 Hz, 1H), 5.05 (s, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.2, 164.0, 162.7, 149.9, 137.3, 125.7, 124.5, 120.3, 62.1, 60.9, 14.3.

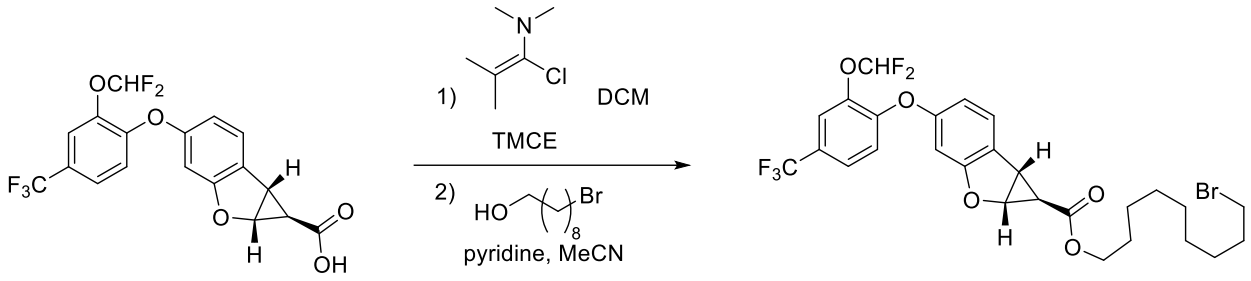
Ethyl 4-(((4-bromobutanoyl)oxy)methyl)-2-(pyridin-2-yl)thiazole-5-carboxylate (S3). 43% yield (358 mg, 0.86 mmol). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (ddd, *J* = 4.8, 1.7, 0.9 Hz, 1H), 8.21 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.82 (td, *J* = 7.8, 1.7 Hz, 1H), 7.38 (ddd, *J* = 7.6, 4.8, 1.2 Hz, 1H), 5.60 (s, 2H), 4.38 (q, *J* = 7.1 Hz, 2H), 3.53 (t, *J* = 6.5 Hz, 2H), 2.63 (t, *J* = 7.1 Hz, 2H), 2.25 (tt, *J* = 6.8, 6.8 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.2, 171.7, 161.5, 157.5, 150.6, 149.8, 137.3, 126.8, 125.7, 120.4, 61.9, 60.8, 32.8, 32.5, 28.0, 14.3. HRMS (ESI^+): calculated for $C_{16}H_{17}BrN_2O_4SNa^+$: 434.9985, found 434.9969.



Indomethacin (1.0 equiv., 0.8 mmol, 287 mg) was dissolved in 8 ml dry dichloromethane in the N_2 glovebox. Tetramethyl-α-chloro-enamine (TMCE, 1.5 equiv. 1.2 mmol, 161 mg) was added in the solution. The reaction mixture was stirred for 3 h at room temperature then was concentrated in vacuo to a yellow solid. The crude solid was redissolved in acetonitrile, followed by addition of 9-nonanol-1-bromide (1.5 equiv., 1.2 mmol, 268 mg) and pyridine (1.5 equiv., 1.2

mmol, 95 mg). The reaction mixture was stirred for 3 h at room temperature, and then concentrated in vacuo. The crude residue was purified by flash chromatography on silica gel (230-400 mesh) with ethyl acetate/hexane (5 – 20% gradient), affording the product in 85% yield (405 mg, 0. 72 mmol) as a yellow oily solid.

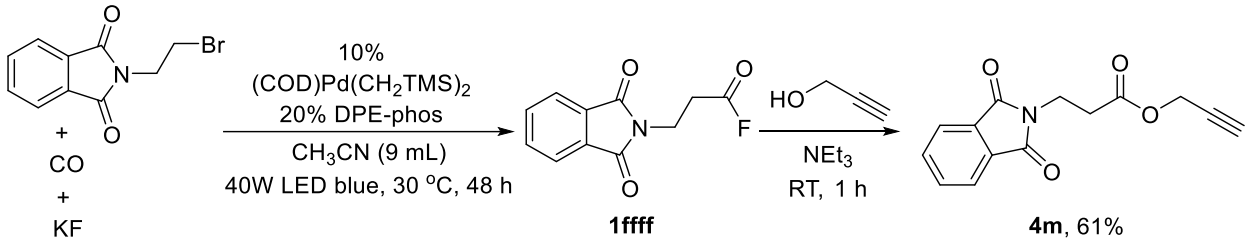
9-bromononyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate (S4). 85% yield (405 mg, 0. 72 mmol). Yellow oily solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.5 Hz, 2H), 7.47 (d, *J* = 8.5 Hz, 2H), 6.97 (d, *J* = 2.5 Hz, 1H), 6.87 (d, *J* = 9.0 Hz, 1H), 6.67 (dd, *J* = 9.0, 2.6 Hz, 1H), 4.09 (t, *J* = 6.7 Hz, 2H), 3.84 (s, 3H), 3.65 (s, 2H), 3.40 (t, *J* = 6.8 Hz, 2H), 2.39 (s, 3H), 1.88 – 1.79 (m, 2H), 1.60 (q, *J* = 6.9 Hz, 2H), 1.40 (tt, *J* = 9.2, 4.6 Hz, 2H), 1.33 – 1.23 (m, 8H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.0, 168.4, 156.1, 139.4, 136.0, 134.0, 131.3, 130.9, 130.8, 129.2, 115.0, 112.8, 111.7, 101.4, 65.2, 55.8, 34.1, 32.9, 30.6, 29.4, 29.2, 28.7, 28.7, 28.2, 25.9, 13.5. HRMS (ESI$^+$): calculated for $C_{28}H_{33}NO_4BrClNa^+$: 584.1174, found 584.1148.



(1*R*,1a*R*,6b*S*)-4-(2-(trifluoromethoxy)-4-(trifluoromethyl)phenoxy)-1a,6b-dihydro-1*H*-cyclopropa[*b*]benzofuran-1-carboxylic acid (1.0 equiv., 0.85 mmol, 357 mg) was dissolved in 6 ml dry dichloromethane in the N_2 glovebox. The tetramethyl-α-chloro-enamine(TMCE, 1.76 equiv., 1.5 mmol, 201 mg) was added in the solution. The reaction mixture was stirred for 3 h at room temperature, and then concentrated in vacuo as a yellow oil. The crude solid was redissolved in acetonitrile, followed by addition of 9-bromononanol (1.5 equiv., 1.3 mmol, 348 mg) and pyridine (1.5 equiv., 1.3 mmol, 123 mg). The reaction mixture was stirred for 3 h at room temperature, and then concentrated in vacuo. The crude residue was purified by flash chromatography on silica gel (230-400 mesh) with ethyl acetate/hexane (0 – 20% gradient), affording the product in 95% yield (505 mg, 0.81 mmol) as a colorless thick oil.

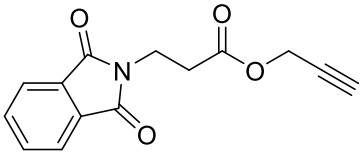
9-bromononyl (1*R*,1a*R*,6b*S*)-4-(2-(difluoromethoxy)-4-(trifluoromethyl)phenoxy)-1a,6b-dihydro-1*H*-cyclopropa[*b*]benzofuran-1-carboxylate (S5). 95% yield (505 mg, 0.81 mmol). Colorless thick oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 2.2 Hz, 1H), 7.42 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 6.99 (d, *J* = 8.6 Hz, 1H), 6.64 – 6.56 (m, 3H), 5.12 (dd, *J* = 5.5, 1.1 Hz, 1H), 4.11 (td, *J* = 6.7, 1.3 Hz, 2H), 3.53 (dd, *J* = 6.7, 6.7 Hz, 1H), 3.41 (t, *J* = 6.9 Hz, 2H), 3.26 (dd, *J* = 5.6, 3.1 Hz, 1H), 1.90 – 1.78 (m, 2H), 1.64 (p, *J* = 6.7 Hz, 2H), 1.42 (q, *J* = 7.1 Hz, 2H), 1.37 – 1.23 (m, 8H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.6, 160.8, 155.8, 151.7, 141.0 (t, *J* = 2.8 Hz), 126.1 (q, *J* = 32.1 Hz), 125.0, 124.8, 123.91 (q, *J* = 3.8 Hz), 123.7 (q, *J* = 272.3 Hz), 120.59 (d, *J* = 3.9 Hz), 119.5, 115.51 (t, *J* = 263.8 Hz), 112.0, 102.4, 68.2, 65.2, 34.0, 32.7, 29.6, 29.2, 29.1, 28.6, 28.6, 28.1, 25.8, 23.7. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.0, -81.8. HRMS (ESI^+): calculated for $C_{27}H_{28}BrF_5NO_5^+$: 629.0932, found 629.0933.

7. Typical carbonylative couplings with nucleophilic trapping (Figure 5b)



In a glovebox, 2-(2-bromoethyl)isoindoline-1,3-dione (76.2 mg, 0.30 mmol), $(COD)Pd(CH_2TMS)_2$ (11.7 mg, 0.03 mmol), DPE-Phos (32.3 mg, 0.06 mmol) and 1,2-dichloroethane (9.9 mg, 0.1 mmol) were dissolved in 4 mL of CH_3CN. The mixture was transferred into a thick-walled 25 mL glass reaction vessel equipped with a magnetic stir bar and a Teflon cap. A suspension of potassium fluoride (34.9 mg, 0.60 mmol), was prepared in 2 mL CH_3CN and transferred to the vessel. The vessel was closed, taken out of the glovebox and attached to a CO line. Before opening the vessel, the connecting tubing was evacuated and backfilled with carbon monoxide three times, and finally, the vessel was opened and pressurized with 4 atm carbon monoxide (on top of 1 atm of nitrogen). The vessel was closed and clamped on top of a stirring plate, and the solution was irradiated using a 40W Blue LED lamp. Fans were used to keep the temperature below 30 ºC (see the picture of setup in Figure S5A). After 48 hours, the vessel was

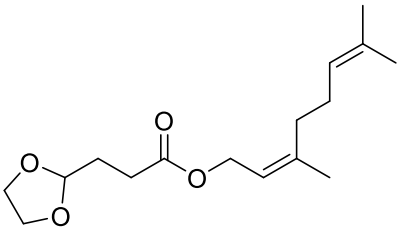
taken out of the irradiation system and attached to a Schlenk line in a well-ventilated fume hood. The cap was slowly opened under N_2 flow to release the excess CO. Under N_2 flow, propargyl alcohol (25.2 mg, 0.45 mmol) solution in dichloromethane (0.5 mL) was quickly added *via* syringe, followed by the addition of NEt_3 (0.08 mL, 0.6 mmol). The mixture was stirred at room temperature for 1 h. The product was isolated by column: gradient ethyl acetate/hexane = 10-20%, affording **4e** as a pale-yellow liquid in 61% yield (47.0 mg, 0.18 mmol).



Prop-2-yn-1-yl 3-(1,3-dioxoisoindolin-2-yl)propanoate (4m). 61% yield (47.0 mg, 0.18 mmol), pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.72 (dd, *J* = 5.5, 3.0 Hz, 2H), 4.68 (d, *J* = 2.4 Hz, 2H), 4.02 (t, *J* = 7.2 Hz, 2H), 2.79 (t, *J* = 7.2 Hz, 2H), 2.44 (t, *J* = 2.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.0, 168.0, 134.1, 132.0, 123.4, 77.3, 75.1, 52.3, 33.6, 32.7. HRMS: calculated for $C_{14}H_{11}NO_4Na^+$ ($M+Na^+$): 280.0580, found: 280.0584.

Compounds **4m-v** were obtained using similar procedures as described above to build-up the acyl fluorides, but with the following modifications in the reaction with nucleophiles. The reaction conditions with nucleophiles are adapted from the literature.[9-12]

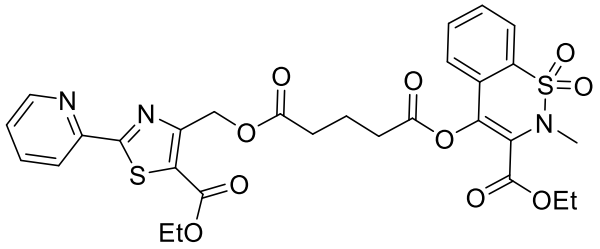
4n: Nerol (69.4 mg, 0.45 mmol), NEt_3 (0.08 mL, 0.6 mmol), room temperature, 6 h. The product was isolated by column: ethyl acetate/hexane = 10%.



(*Z*)-3,7-dimethylocta-2,6-dien-1-yl 3-(1,3-dioxolan-2-yl)propanoate (4n). 63% NMR yield, 40% isolated yield (36.4 mg, 0.13 mmol), colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.35 (td, *J* = 7.2, 1.6 Hz, 1H), 5.08 (tdd, *J* = 7.0, 1.5, 1.5 Hz, 1H), 4.94 (t, *J* = 4.3 Hz, 1H), 4.57 (dd, *J* = 7.2, 0.6 Hz, 2H), 3.99 – 3.90 (m, 2H), 3.90 – 3.79 (m, 2H), 2.43 (t, *J* = 7.6 Hz, 2H), 2.14 – 2.04 (m, 4H), 2.01 (td, *J* = 7.6, 4.3 Hz, 2H), 1.76 (d, *J* = 1.2 Hz, 3H), 1.68 (d, *J* = 1.4 Hz, 3H), 1.60 (d, *J* = 1.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.2, 142.5, 132.2, 123.6, 119.2, 103.2, 65.0, 61.1, 32.2, 28.9, 28.4, 26.7, 25.7, 23.5, 17.7. HRMS: calculated for $C_{16}H_{26}O_4Na^+$ ($M+Na^+$): 305.1723, found: 305.1713.

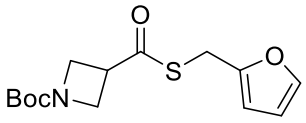
4o: 0.2 mmol alkyl bromide was used to start. ethyl 4-hydroxy-2-methyl-2H-benzo[e][1,2]thiazine-3-carboxylate 1,1-dioxide (114 mg, 0.40 mmol), ^{i}Pr$_2$EtN (0.07 mL, 0.40

mmol), room temperature, 2 h. The product was isolated by column: gradient ethyl acetate/hexane = 10-80%.



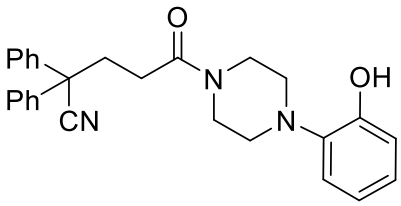
(5-(ethoxycarbonyl)-2-(pyridin-2-yl)thiazol-4-yl)methyl (3-(ethoxycarbonyl)-2-methyl-1,1-dioxido-2H-benzo[e][1,2]thiazin-4-yl) glutarate (4o). 48% NMR yield, 28% isolated yield (35.8 mg, 0.06 mmol). Pale orange solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 4.8 Hz, 1H), 8.18 (d, *J* = 8.0 Hz, 1H), 7.92 – 7.85 (m, 1H), 7.75 (ddd, *J* = 9.4, 7.7, 1.7 Hz, 1H), 7.68 – 7.59 (m, 2H), 7.56 – 7.46 (m, 1H), 7.33 (ddd, *J* = 7.6, 4.8, 1.2 Hz, 1H), 5.63 (s, 2H), 4.37 (q, *J* = 7.2 Hz, 2H), 4.30 (q, *J* = 7.2 Hz, 2H), 3.13 (s, 3H), 2.89 (t, *J* = 7.4 Hz, 2H), 2.63 (t, *J* = 7.1 Hz, 2H), 2.19 (tt, *J* = 7.2 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 4H), 1.34 (t, *J* = 7.1 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.4, 171.7, 170.5, 161.4, 160.9, 157.5, 150.3, 149.6, 144.5, 137.2, 134.6, 132.3, 131.7, 128.5, 126.7, 125.8, 125.6, 125.1, 123.1, 120.2, 62.1, 61.8, 60.6, 37.4, 32.9, 32.8, 19.8, 14.2, 14.1. HRMS (ESI^+): calculated for $C_{29}H_{29}N_3O_{10}S_2Na^+$ ($M+Na^+$): 666.1192, found: 666.1183.

4p: Furfuryl mecaptan (68.5 mg, 0.6 mmol), $^{i}Pr_2EtN$ (0.10 mL, 0.6 mmol), room temperature, 2 h. The product was isolated by column: gradient ethyl acetate/hexane = 5-20%.



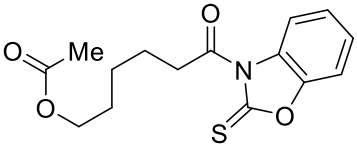
Tert-butyl 3-(((furan-2-ylmethyl)thio)carbonyl)azetidine-1-carboxylate (4p). 66% yield (58.7 mg, 0.20 mmol), yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 1.9, 0.9 Hz, 1H), 6.30 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.27 – 6.19 (m, 1H), 4.21 (s, 2H), 4.12 (dd, *J* = 8.7, 6.2 Hz, 2H), 4.08 (dd, *J* = 8.7, 8.7 Hz, 2H), 3.54 (tt, *J* = 8.6, 6.1 Hz, 1H), 1.43 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.2, 156.0, 149.8, 142.4, 110.7, 108.3, 80.0, 51.8 (br), 39.9, 28.4, 25.8. HRMS: calculated for $C_{14}H_{19}NO_4SNa^+$ ($M+Na^+$): 320.0927, found: 320.0940.

4q: 1-(3-Hydroxyphenyl)piperazine (107 mg, 0.6 mmol), $^{i}Pr_2EtN$ (0.10 mL, 0.6 mmol), room temperature, 4 h. The product was isolated by column: gradient ethyl acetate/hexane = 20-60%.



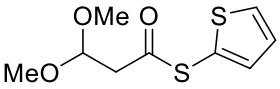
5-(4-(2-Hydroxyphenyl)piperazin-1-yl)-5-oxo-2,2-diphenylpentanenitrile (4q). 60% yield (76.4 mg, 0.18 mmol), colorless solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.6 Hz, 4H), 7.37 (t, *J* = 7.6 Hz, 4H), 7.31 (t, *J* = 7.2 Hz, 2H), 7.12 (t, *J* = 8.0 Hz, 1H), 6.47 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.40 – 6.33 (m, 2H), 5.06 (s, 1H), 3.73 (t, *J* = 5.2 Hz, 2H), 3.50 (t, *J* = 5.1 Hz, 2H), 3.11 (dt, *J* = 10.3, 5.5 Hz, 4H), 2.86 – 2.76 (m, 2H), 2.53 – 2.42 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.7, 156.7, 152.3, 139.5, 130.2, 129.1, 128.1, 126.8, 122.2, 109.0, 107.4, 103.5, 51.1, 49.3, 49.0, 45.2, 41.6, 34.7, 29.5. HRMS: calculated for $C_{27}H_{27}N_3O_2Na^+$ ($M+Na^+$): 448.1995, found: 448.1988.

4r: Mercaptobenzoxazole (138 mg, 0.6 mmol), $^{i}Pr_2EtN$ (0.10 mL, 0.6 mmol), room temperature, 4 h. The product was isolated by column: ethyl acetate/hexane = 10%. The product is not very stable over silica.



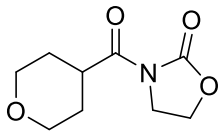
6-(Benzo[d]oxazol-2-ylthio)-6-oxohexyl acetate (4r). 94% NMR yield, 34% isolated yield (29.4 mg, 0.10 mmol), yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.40 – 7.28 (m, 3H), 4.10 (t, *J* = 6.6 Hz, 2H), 3.53 (t, *J* = 7.3 Hz, 2H), 2.05 (s, 3H), 1.88 (tt, *J* = 7.6, 7.4 Hz, 2H), 1.72 (tt, *J* = 7.6, 6.9 Hz, 2H), 1.52 (tt, 8.1, 7.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.8, 173.9, 171.2, 146.6, 130.0, 126.1, 125.6, 116.5, 109.7, 64.2, 39.1, 28.4, 25.4, 23.9, 21.0. HRMS: calculated for $C_{15}H_{17}N_5SNa^+$ ($M+Na^+$): 330.0770, found: 330.0776.

4s: 2-mercaptothiophene (52.3 mg, 0.45 mmol), $^{i}Pr_2EtN$ (0.10 mL, 0.6 mmol), room temperature, 2 h. The product was isolated by column: ethyl acetate/hexane = 5%.

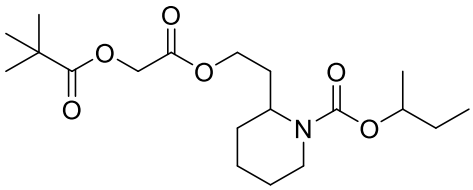


S-(thiophen-2-yl) 3,3-dimethoxypropanethioate (4s). 56% NMR yield, 48% isolated yield (33.7 mg, 0.14 mmol), colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (td, *J* = 5.2, 1.3 Hz, 1H), 7.18 (td, *J* = 3.7, 1.3 Hz, 1H), 7.11 (ddd, *J* = 5.5, 3.6, 1.8 Hz, 1H), 4.85 (t, *J* = 5.6 Hz, 1H), 3.38 (s, 6H), 2.96 (d, *J* = 5.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.8, 135.9, 132.0, 127.9, 124.4, 101.1, 53.9, 46.7. HRMS: calculated for $C_9H_{12}O_3S_2Na^+$ ($M+Na^+$): 255.0120, found: 255.0122.

4t: oxazolidinone (52.2 mg, 0.6 mmol), DMAP (73.3 mg, 0.6 mmol), 90 °C, 24 h. The product was isolated by column: gradient ethyl acetate/hexane = 10-30%.

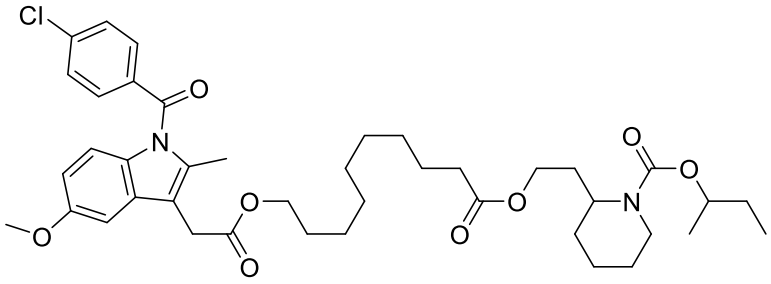


3-(Tetrahydro-2H-pyran-4-carbonyl)oxazolidin-2-one (4t). 70% yield (42.0 mg, 0.21 mmol), yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.42 (t, *J* = 8.4 Hz, 2H), 4.02 (t, *J* = 8.3 Hz, 2H), 4.02 – 3.96 (m, 2H), 3.74 (tt, *J* = 10.9, 4.2 Hz, 1H), 3.49 (td, *J* = 11.5, 2.8 Hz, 2H), 1.88 – 1.72 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.0, 153.2, 67.1, 62.1, 42.8, 39.3, 28.6. HRMS: calculated for $C_9H_{13}NO_4Na^+$ ($M+Na^+$): 222.0737, found: 222.0734.**4u**: Icaridin (227 mg, 1.5 mmol), $^{i}Pr_2EtN$ (0.10 mL, 0.6 mmol), room temperature, 2 h. The product was isolated by column: gradient ethyl acetate/hexane = 10-20%.



Sec-butyl-2-(2-(2-(pivaloyloxy)acetoxy)ethyl) piperidine-1-carboxylate (4u). 41% yield (46.0 mg, 0.12 mmol), bright yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.74 (qt, *J* = 6.3, 3.0 Hz, 1H), 4.59 (s, 2H), 4.40 (br s, 1H), 4.22 – 4.09 (m, 2H), 4.09 – 3.95 (m, 1H), 2.79 (t, *J* = 12.9 Hz, 1H), 2.16 – 2.05 (m, 1H), 1.79 – 1.70 (m, 1H), 1.63 – 1.49 (m, 6H), 1.47 – 1.34 (m, 1H), 1.25 (s, 8H), 1.20 (dd, *J* = 6.3, 1.5 Hz, 3H), 0.90 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.9, 167.9, 155.5, 73.0, 62.9, 60.6, 47.7, 38.9, 38.7, 29.1, 28.7, 27.1 (two signals overlapped), 25.5, 19.8, 19.0, 9.7. HRMS: calculated for $C_{19}H_{33}NO_6Na^+$ ($M+Na^+$): 394.2200, found: 394.2203.

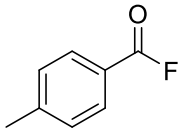
4v: Icaridin (227 mg, 1.5 mmol), $^{i}Pr_2EtN$ (0.10 mL, 0.6 mmol), room temperature, 2 h. The product was isolated by column: gradient ethyl acetate/hexane = 0-20%.



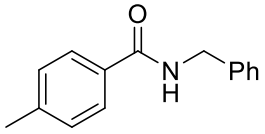
***sec*-butyl 2-(2-((10-(2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetoxy) decanoyl)oxy)ethyl)piperidine-1-carboxylate (4v).** 81% (120 mg, 0.162 mmol). Yellow oil. ^{1}H NMR (800 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.5 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 6.96 (d, *J* = 2.6

Hz, 1H), 6.86 (d, *J* = 9.0 Hz, 1H), 6.65 (dd, *J* = 9.0, 2.5 Hz, 1H), 4.73 (ddt, *J* = 9.2, 6.4, 2.9 Hz, 1H), 4.40 (brs, 1H), 4.08 (t, *J* = 6.8 Hz, 2H), 4.06 – 4.03 (m, 2H), 3.82 (s, 3H), 3.64 (s, 2H), 2.80 (brt, *J* = 13.4 Hz, 1H), 2.37 (s, 3H), 2.27 (t, *J* = 7.6 Hz, 2H), 2.09 – 2.06 (m, 1H), 1.77 – 1.70 (m, 1H), 1.64 – 1.48 (m, 12fH), 1.44 – 1.40 (m, 1H), 1.29 – 1.22 (m, 8H), 1.19 (dd, *J* = 6.3, 1.8 Hz, 3H), 0.89 (brt, *J* = 7.8 Hz, 3H). ^{13}C NMR (201 MHz, $CDCl_3$) δ 173.8, 171.0, 168.3, 156.1, 155.5, 139.3, 135.9, 134.0, 131.2, 130.9, 130.7, 129.2, 115.0, 112.8, 111.7, 101.4, 72.9, 65.2, 62.0, 62.0, 55.7, 34.3, 30.5, 29.4, 29.2, 29.2, 29.2, 29.1, 28.7, 25.9, 25.6, 25.5, 24.9, 19.9, 19.8, 19.2, 19.1, 13.4, 9.8. HRMS (ESI^+): calculated for $C_{41}H_{55}ClN_2O_8Na^+$: 761.3539, found 761.3561.

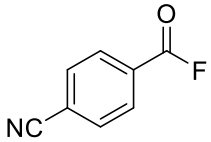
7.1 Characterization data on acid fluorides and their isolated *N*-benzylamides.



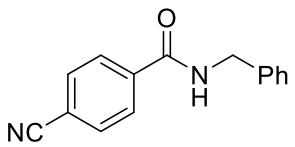
4-Methylbenzoyl fluoride (1d). Spectral data correlated with that previously reported in the literature.[8] *In situ* NMR data: ^{1}H NMR (500 MHz, CD_3CN) δ 7.94 (d, J = 8.3 Hz, 2H), 7.42 (d, J = 4.7 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (126 MHz, CD_3CN) δ 157.5 (d, J = 341.7 Hz), 147.3, 131.4 (d, J = 4.1 Hz), 130.0, 121.8 (d, J = 61.4 Hz), 21.0.^{19}F NMR (471 MHz, CD_3CN) δ 15.95.



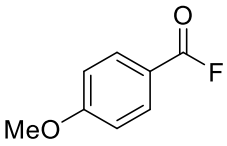
***N*-benzyl-4-methylbenzamide (5d).** 83% yield (36.5 mg, 0.17 mmol). Pale yellow solid. Spectral data correlated with that previously reported in the literature.[13] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 4.4 Hz, 4H), 7.33 – 7.27 (m, 1H), 7.23 (d, *J* = 7.8 Hz, 2H), 6.34 (s, 1H), 4.65 (d, *J* = 5.6 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.2, 142.0, 138.3, 131.5, 129.3, 128.8, 128.0, 127.6, 127.0, 44.1, 21.5.



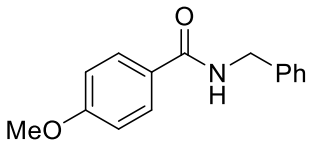
4-Cyanobenzoyl fluoride (1e). 92% NMR yield, 22% Isolated yield (33.4 mg, 0.22 mmol/1.0 mmol), white solid. Spectral data correlated with that previously reported in the literature.[14] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.4 Hz, 2H), 7.85 (dt, *J* = 8.0, 1.1 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.7 (d, *J* = 346.1 Hz), 132.8, 131.8 (d, *J* = 3.6 Hz), 128.8 (d, *J* = 63.4 Hz), 118.8, 117.2. ^{19}F NMR (471 MHz, $CDCl_3$) δ 20.23.



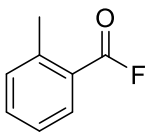
***N*-benzyl-4-cyanobenzamide (5e).** 95% yield (44.8 mg, 0.19 mmol/0.2 mmol); 92% (216 mg, 0.92 mmol/1 mmol). Colorless solid. Spectral data correlated with that previously reported in the literature.[15] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.5 Hz, 2H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.39 – 7.27 (m, 5H), 6.78 (s, 1H), 4.61 (d, *J* = 5.7 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.6, 138.3, 137.6, 132.4, 128.9, 127.9, 127.9, 127.8, 118.0, 115.1, 44.3.



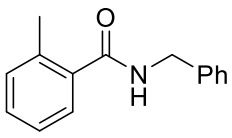
4-Methoxybenzoyl fluoride (1f). 81% NMR yield, 32%Isolated yield (10.0 mg, 0.06 mmol/0.2 mmol), Colorless oil. Spectral data correlated with that previously reported in the literature.[16] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.9 Hz, 2H), 6.99 (dd, *J* = 8.7, 1.4 Hz, 2H), 3.90 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.2, 157.3 (d, *J* = 340.0 Hz), 133.8 (d, *J* = 4.1 Hz), 116.9 (d, *J* = 61.7 Hz), 114.4, 55.7. ^{19}F NMR (471 MHz, $CDCl_3$) δ 15.98.



***N*-benzyl-4-methoxybenzamide (5f).** 83% yield (36.5 mg, 0.17 mmol). Yellow solid. Spectral data correlated with that previously reported in the literature.[17] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.9 Hz, 2H), 7.36 (d, *J* = 4.6 Hz, 4H), 7.33 – 7.28 (m, 1H), 6.92 (d, *J* = 8.9 Hz, 2H), 6.29 (s, 1H), 4.64 (d, *J* = 5.6 Hz, 2H), 3.85 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.8, 162.2, 138.4, 135.0, 128.8, 128.8, 128.0, 127.6, 126.7, 113.8, 55.4, 44.1.

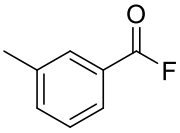


2-Methylbenzoyl fluoride (1g). Spectral data correlated with that previously reported in the literature.[18] *In situ* NMR data: ^{1}H NMR (400 MHz, CD_3CN) δ 8.00 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.63 (ddd, *J* = 7.6, 7.5, 1.4 Hz, 1H), 7.46 – 7.38 (m, 2H), 2.62 (d, *J* = 1.9 Hz, 3H). ^{13}C NMR (126 MHz, CD_3CN) δ 156.7 (d, *J* = 344.7 Hz), 143.4 (d, *J* = 6.9 Hz), 135.0, 132.3 (dd, *J* = 8.1, 3.2 Hz), 128.6 (d, *J* = 88.3 Hz), 126.5, 123.4 (d, *J* = 57.1 Hz), 20.9 (d, *J* = 1.7 Hz). ^{19}F NMR (377 MHz, CD_3CN) δ 28.03.

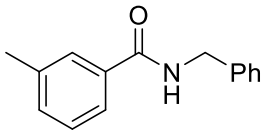


***N*-benzyl-2-methylbenzamide (5g).** 90% yield (40.6 mg, 0.19 mmol). Beige solid. Spectral data correlated with that previously reported in the literature.[19] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 5H), 7.33 – 7.28 (m, 2H), 7.25 – 7.19 (m, 2H), 7.22 – 7.15 (m, 1H), 6.03 (s, 1H), 4.63 (d, *J* = 5.8 Hz, 2H), 2.47 (s, 3H). ^{13}C NMR

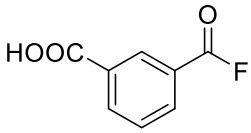
(126 MHz, $CDCl_3$) δ 169.9, 138.2, 136.3, 136.2, 131.1, 130.0, 128.8, 127.9, 127.6, 126.7, 125.8, 44.0, 19.9.



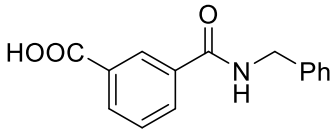
3-Methylbenzoyl fluoride (1h). Spectral data correlated with that previously reported in the literature.[8] *In situ* NMR data: ^{1}H NMR (500 MHz, CD_3CN) δ 7.88 (s, 1H), 7.85 (d, *J* = 7.6 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.48 (ddd, *J* = 7.7, 7.6, 1.3 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (126 MHz, CD_3CN) δ 157.6 (d, *J* = 343.3 Hz), 139.6, 136.4, 131.6 (d, *J* = 4.1 Hz), 129.2, 128.4 (d, *J* = 4.0 Hz), 124.6 (d, *J* = 60.4 Hz), 20.2. ^{19}F NMR (471 MHz, CD_3CN) δ 16.82.



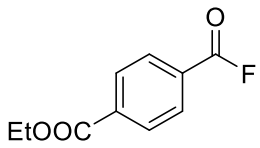
***N*-benzyl-3-methylbenzamide (5h).** 84% yield (37.9 mg, 0.17 mmol). Pale yellow solid. Spectral data correlated with that previously reported in the literature.[20] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 – 7.60 (m, 1H), 7.56 (ddd, *J* = 5.0, 3.9, 1.9 Hz, 1H), 7.36 (d, *J* = 4.4 Hz, 4H), 7.33 – 7.29(m, 3H), 6.37 (s, 1H), 4.65 (d, *J* = 5.7 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.5, 138.5, 138.2, 134.4, 132.3, 128.8, 128.5, 128.0, 127.7, 127.6, 123.9, 44.2, 21.4.



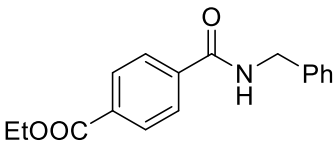
3-(Fluorocarbonyl)benzoic acid (1i). *In situ* NMR data: ^{1}H NMR (500 MHz, CD_3CN) δ 13.02 (br s, 1H), 8.60 (s, 1H), 8.37 (d, *J* = 7.8 Hz, 1H), 8.16 (d, *J* = 7.8 Hz, 1H), 7.66 (overlapped with TBDS, m, 1H). ^{13}C NMR (126 MHz, CD_3CN) δ 166.9, 157.1 (d, *J* = 343.7 Hz), 137.6 (d, *J* = 3.7 Hz), 136.2, 134.1 (d, *J* = 3.9 Hz), 129.4, 128.5, 124.9 (d, *J* = 61.9 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ 17.40.



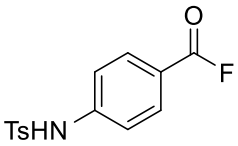
3-(Benzylcarbamoyl)benzoic acid (5i). 50% yield (25.7 mg, 0.10 mmol). Colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (t, *J* = 1.8 Hz, 1H), 8.48 (s, 1H), 8.18 (ddt, *J* = 7.9, 6.9, 1.4 Hz, 2H), 7.61 (t, *J* = 7.8 Hz, 1H), 7.45 – 7.37 (m, 2H), 7.37 – 7.29 (m, 2H), 7.29 – 7.19 (m, 1H), 4.64 (d, *J* = 6.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 166.6, 140.7, 136.3, 133.2, 132.7, 132.1, 129.7, 129.3, 128.6, 127.9, 44.2. HRMS: calculated for $C_{15}H_{13}NO_3Na^+$ ($M+Na^+$): 278.0788, found: 278.0790.



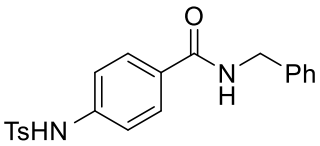
Ethyl 4-(fluorocarbonyl)benzoate (1j). Spectral data correlated with that previously reported in the literature.[10] *In situ* NMR data: ^{1}H NMR (400 MHz, CD_3CN) δ 8.17 (d, *J* = 8.7 Hz, 2H), 8.13 (d, *J* = 8.7 Hz, 2H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.37 (overlapped with TBDS, 3H). ^{13}C NMR (126 MHz, CD_3CN) δ 165.0, 156.8 (d, *J* = 344.7 Hz), 136.6, 131.5 (d, *J* = 3.7 Hz), 129.8, 128.4 (d, *J* = 61.9 Hz), 61.7, 13.5 ^{19}F NMR (377 MHz, CD_3CN) δ 18.54.



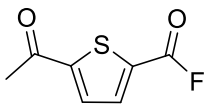
Ethyl 4-(benzylcarbamoyl)benzoate (5j). 99% yield (283 mg, 1.0 mmol). Colorless solid. Spectral data correlated with that previously reported in the literature.[21] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.5 Hz, 2H), 7.84 (d, *J* = 8.5 Hz, 2H), 7.39 – 7.33 (m, 4H), 7.34 – 7.27 (m, 1H), 6.54 (s, 1H), 4.65 (d, *J* = 5.7 Hz, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.5, 165.8, 138.2, 137.9, 133.2, 129.8, 128.9, 128.0, 127.8, 127.0, 61.4, 44.3, 14.3.



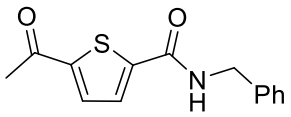
4-((4-Methylphenyl)sulfonamido)benzoyl fluoride (1k). *In situ* NMR data: ^{1}H NMR (500 MHz, CD_3CN) δ 7.74 (d, 2H, overlapped with TBDS), 7.62 (d, *J* = 7.8 Hz, 2H), 7.26 (d, *J* = 6.6 Hz, 2H), 7.20 (d, *J* = 7.7 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (126 MHz, CD_3CN) δ 158.1 (d, *J* = 332.8 Hz), 143.5, 140.5, 139.6, 137.5, 132.4 (d, *J* = 4.1 Hz), 129.5, 128.8, 126.5, 20.5. ^{19}F NMR (377 MHz, CD_3CN) δ 9.93.



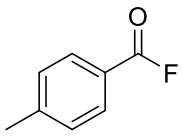
***N*-benzyl-4-((4-methylphenyl)sulfonamido)benzamide (5k).** 62% yield (47.3 mg, 0.12 mmol). Pale yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 – 7.61 (m, 4H), 7.37 – 7.27 (m, 5H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.6 Hz, 2H), 6.93 (br s, 1H), 6.28 (t, *J* = 5.5 Hz, 1H), 4.61 (d, *J* = 5.6 Hz, 2H), 2.37 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.4, 144.3, 139.8, 138.0, 135.8, 130.6, 129.8, 128.8, 128.4, 128.0, 127.7, 127.2, 120.0, 44.2, 21.6. HRMS: calculated for $C_{21}H_{20}N_2O_3SNa^+$ ($M+Na^+$): 403.1090, found: 403.1087.



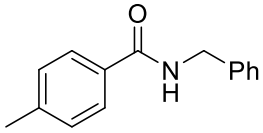
5-Acetylthiophene-2-carbonyl fluoride (1l). *In situ* NMR data: ^{1}H NMR (500 MHz, CD_3CN) δ 7.99 (d, *J* = 4.0 Hz, 1H), 7.83 (dd, *J* = 4.0, 2.0 Hz, 1H), 2.59 (s, 3H). ^{13}C NMR (126 MHz, CD_3CN) δ 191.3, 152.7, 152.7, 152.2 (d, *J* = 334.2 Hz), 138.4 (d, *J* = 2.6 Hz), 132.9. ^{19}F NMR (471 MHz, CD_3CN) δ 23.82.



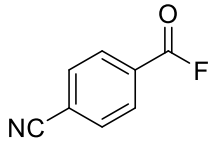
5-Acetyl-*N*-benzylthiophene-2-carboxamide (5l). 99% yield (51.2 mg, 0.20 mmol). Beige solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 3.9 Hz, 1H), 7.52 (d, *J* = 3.9 Hz, 1H), 7.40 – 7.27 (m, 5H), 6.41 (s, 1H), 4.62 (d, *J* = 5.8 Hz, 2H), 2.56 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.7, 161.0, 146.8, 144.8, 137.5, 132.0, 128.9, 128.9, 128.0, 127.9, 44.27, 27.0. HRMS: calculated for $C_{14}H_{13}NO_2SNa^+$ ($M+Na^+$): 282.0553, found: 282.0559.



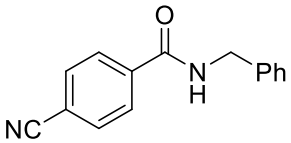
4-Methylbenzoyl fluoride (1m). NMR data are the same as **1d**. Spectral data correlated with that previously reported in the literature.[8] *In situ* NMR data: ^{1}H NMR (500 MHz, CD_3CN) δ 7.94 (d, J = 8.3 Hz, 2H), 7.42 (d, J = 4.7 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (126 MHz, CD_3CN) δ 157.5 (d, J = 341.7 Hz), 147.3, 131.4 (d, J = 4.1 Hz), 130.0, 121.8 (d, J = 61.4 Hz), 21.0.^{19}F NMR (471 MHz, CD_3CN) δ 15.95.



***N*-benzyl-4-methylbenzamide (5m).** 75% yield (33.0 mg, 0.15 mmol). Pale yellow solid. NMR data are the same as **5d**. Spectral data correlated with that previously reported in the literature.[13] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 4.4 Hz, 4H), 7.33 – 7.27 (m, 1H), 7.23 (d, *J* = 7.8 Hz, 2H), 6.34 (s, 1H), 4.65 (d, *J* = 5.6 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.2, 142.0, 138.3, 131.5, 129.3, 128.8, 128.0, 127.6, 127.0, 44.1, 21.5.

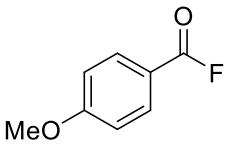


4-Cyanobenzoyl fluoride (1n). Spectral data correlated with that previously reported in the literature.[14] *In situ* NMR data: ^{1}H NMR (500 MHz, CD_3CN) δ 8.16 (d, *J* = 8.3 Hz, 2H), 7.94 (dt, *J* = 8.1, 1.2 Hz, 2H). ^{13}C NMR (126 MHz, CD_3CN) δ 156.2 (d, *J* = 345.2 Hz), 133.1, 131.8 (d, *J* = 3.8 Hz), 128.7 (d, *J* = 63.3 Hz), 118.4, 117.5. ^{19}F NMR (377 MHz, CD_3CN) δ 18.71.

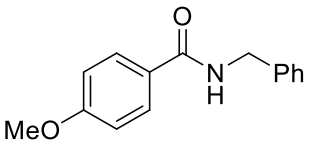


***N*-benzyl-4-cyanobenzamide (5n).** 84% yield (39.6 mg, 0.17 mmol); 69% (160 mg, 0.69 mmol/ 1 mmol). Colorless solid. NMR data are the same as **5e**. Spectral data correlated with that previously reported in the literature.[15] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.5 Hz, 2H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.39

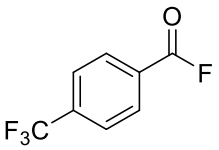
– 7.27 (m, 5H), 6.78 (s, 1H), 4.61 (d, *J* = 5.7 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.6, 138.3, 137.6, 132.4, 128.9, 127.9, 127.9, 127.8, 118.0, 115.1, 44.3.



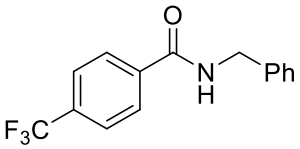
4-Methoxybenzoyl fluoride (1o). Spectral data correlated with that previously reported in the literature.[14] *In situ* NMR data: ^{1}H NMR (500 MHz, CD_3CN) δ 8.06 – 7.94 (m, 2H), 7.08 (dd, *J* = 9.0, 1.4 Hz, 2H), 3.89 (s, 3H). ^{13}C NMR (126 MHz, CD_3CN) δ 165.6, 157.2 (d, *J* = 338.3 Hz), 133.7 (d, *J* = 4.1 Hz), 116.4 (d, *J* = 62.3 Hz), 114.7, 55.7. ^{19}F NMR (377 MHz, CD_3CN) δ 14.48.



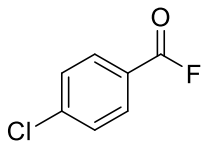
***N*-benzyl-4-methoxybenzamide (5o).** 72% yield (34.7 mg, 0.14 mmol). Yellow solid. NMR data are the same as **5f**. Spectral data correlated with that previously reported in the literature.[17] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.9 Hz, 2H), 7.36 (d, *J* = 4.6 Hz, 4H), 7.33 – 7.28 (m, 1H), 6.92 (d, *J* = 8.9 Hz, 2H), 6.29 (s, 1H), 4.64 (d, *J* = 5.6 Hz, 2H), 3.85 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.8, 162.2, 138.4, 135.0, 128.8, 128.8, 128.0, 127.6, 126.7, 113.8, 55.4, 44.1.



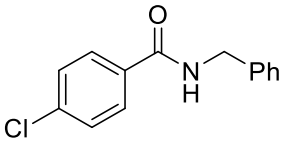
4-(Trifluoromethyl)benzoyl fluoride (1p). Spectral data correlated with that previously reported in the literature.[18, 22] *In situ* NMR data: ^{1}H NMR (500 MHz, CD_3CN) δ 8.22 (d, *J* = 8.2 Hz, 2H), 7.91 (d, *J* = 8.1 Hz, 2H). ^{13}C NMR (126 MHz, CD_3CN) δ 156.4 (d, *J* = 345.1 Hz), 133.9 – 133.2 (m), 132.0 (d, *J* = 3.7 Hz), 128.6 – 128.2 (m), 126.2 (q, *J* = 4.0 Hz), δ 123.6 (d, *J* = 272.4 Hz).^{19}F NMR (377 MHz, CD_3CN) δ 18.63, -63.99.



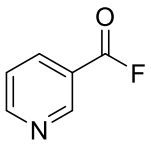
***N*-benzyl-4-(trifluoromethyl)benzamide (5p).** 69% yield (38.6 mg, 0.14 mmol). Colorless solid. Spectral data correlated with that previously reported in the literature.[23] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.2 Hz, 2H), 7.44 – 7.27 (m, 5H), 6.48 (s, 1H), 4.66 (d, *J* = 5.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.0, 137.7, 137.7, δ 133.3 (q, *J* = 32.9 Hz), 128.9, 128.0, 127.9, 127.5, 125.7 (q, *J* = 3.6 Hz), 123.6 (q, *J* = 272.5 Hz), 44.4. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.96.



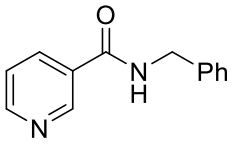
4-Chlorobenzoyl fluoride (1q). Spectral data correlated with that previously reported in the literature [24] *In situ* NMR data: ^{1}H NMR (500 MHz, CD_3CN) δ 8.02 (d, *J* = 8.6 Hz, 2H), 7.61 (dd, *J* = 8.6, 1.4 Hz, 2H). ^{13}C NMR (126 MHz, CD_3CN) δ 156.7 (d, *J* = 342.8 Hz), 141.7, 132.9 (d, *J* = 3.8 Hz), 129.6, 123.5 (d, *J* = 63.1 Hz). ^{19}F NMR (377 MHz, CD_3CN) δ 17.11.



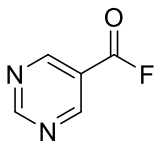
***N*-benzyl-4-chlorobenzamide (5q).** 54% yield (26.5 mg, 0.11 mmol). Colorless solid. Spectral data correlated with that previously reported in the literature.[13] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 – 7.69 (m, 2H), 7.44 – 7.39 (m, 2H), 7.39 – 7.33 (m, 4H), 7.33 – 7.29 (m, 1H), 6.34 (s, 1H), 4.64 (d, *J* = 5.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.2, 137.9, 137.8, 132.8, 128.9 (two signals overlapped), 128.4, 128.0, 127.8, 44.3.



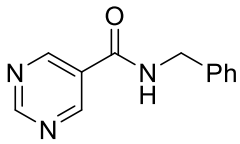
Nicotinoyl fluoride (1r). *In situ* NMR data: ^{1}H NMR (400 MHz, CD_3CN) δ 9.19 (d, *J* = 2.4 Hz, 1H), 8.90 (dd, *J* = 4.9, 1.7 Hz, 1H), 8.34 (ddd, *J* = 8.0, 2.0, 2.0 Hz, 1H), 7.57 (dd, *J* = 8.1, 4.9 Hz, 1H). ^{13}C NMR (126 MHz, CD_3CN) δ 156.5 (d, *J* = 343.7 Hz), 155.7 (d, *J* = 1.7 Hz), 152.0 (d, *J* = 4.2 Hz), 138.8 (d, *J* = 3.8 Hz), 124.2, 121.4 (d, *J* = 61.9 Hz). ^{19}F NMR (377 MHz, CD_3CN) δ 19.08. ^{19}F NMR data matches with literature, no ^{1}H NMR and ^{13}C NMR data reported.[25]



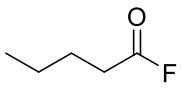
***N*-benzylnicotinamide (5r).** 56% yield (23.9 mg, 0.11 mmol). Pale yellow solid. Spectral data correlated with that previously reported in the literature. [26] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.97 (d, *J* = 1.9 Hz, 1H), 8.70 (dd, *J* = 4.8, 1.7 Hz, 1H), 8.13 (ddd, *J* = 7.9, 4.0, 2.0 Hz, 1H), 7.40 – 7.33 (m, 5H), 7.33 – 7.28 (m, 1H), 6.61 (s, 1H), 4.66 (d, *J* = 5.7 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.5, 152.3, 147.9, 137.7, 135.2, 130.1, 128.9, 128.0, 127.8, 123.5, 44.2.



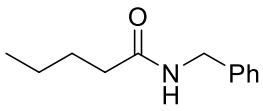
Pyrimidine-5-carbonyl fluoride (1s). *In situ* NMR data: ^{1}H NMR (500 MHz, CD_3CN) δ 9.44 (s, 1H), 9.30 (d, *J* = 0.8 Hz, 2H). ^{13}C NMR (126 MHz, CD_3CN) δ 162.8 (d, *J* = 2.3 Hz), 159.4 (d, *J* = 3.9 Hz), 155.1 (d, *J* = 343.9 Hz), 120.5 (d, *J* = 63.9 Hz). ^{19}F NMR (377 MHz, CD_3CN) δ 21.13.



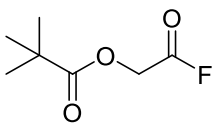
***N*-benzylpyrimidine-5-carboxamide (5s).** 42% yield (18.0 mg, 0.08 mmol). Yellow solid. Spectral data correlated with that previously reported in the literature.[27] ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.29 (s, 1H), 9.10 (s, 2H), 7.40 – 7.29 (m, 5H), 6.62 (s, 1H), 4.65 (d, *J* = 5.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.3, 160.6, 155.6, 137.2, 129.0, 128.1 (two signals overlapped), 127.8, 44.3.



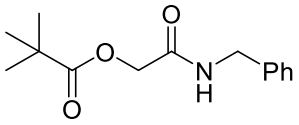
Pentanoyl fluoride (1a). *In situ* NMR data: ^{1}H NMR (500 MHz, CD_3CN) δ 2.56 (td, *J* = 7.4, 0.7 Hz, 2H), 1.66 – 1.56 (m, 2H), 1.43 – 1.32 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, CD_3CN) δ 164.1 (d, *J* = 359.1 Hz), 31.3 (d, *J* = 50.0 Hz), 25.6 (d, *J* = 2.4 Hz), 21.4, 12.8. ^{19}F NMR (471 MHz, CD_3CN) δ 43.06.



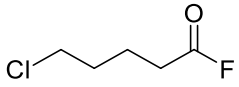
***N*-benzylpentanamide (5a)**. 83% yield (31.9 mg, 0.17 mmol); 90% (168 mg, 0.9 mmol/1 mmol). Colorless solid. Spectral data correlated with that previously reported in the literature.[28] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 2H), 7.31 – 7.25 (m, 3H), 5.70 (s, 1H), 4.44 (d, *J* = 5.7 Hz, 2H), 2.22 (t, *J* = 7.7 Hz, 2H), 1.70 – 1.57 (m, 2H), 1.36 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.0, 138.4, 128.7, 127.8, 127.5, 43.6, 36.8, 27.8, 22.4, 13.8.



2-Fluoro-2-oxoethyl pivalate (1t). *In situ* NMR data: ^{1}H NMR (400 MHz, CD_3CN) δ 4.81 (d, *J* = 3.2 Hz, 2H), 1.23 (s, 9H). ^{13}C NMR (126 MHz, CD_3CN) δ 177.4, 159.2 (d, *J* = 360.3 Hz), 58.5 (d, *J* = 75.0 Hz), 32.7, 26.2. ^{19}F NMR (377 MHz, CD_3CN) δ 27.21.

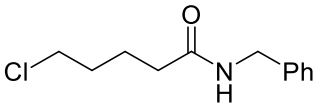


2-(Benzylamino)-2-oxoethyl pivalate (5t). 67% yield (33.5 mg, 0.13 mmol). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.33 (m, 2H), 7.32 – 7.26 (m, 3H), 6.24 (s, 1H), 4.62 (s, 2H), 4.51 (d, *J* = 5.8 Hz, 2H), 1.22 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.9, 167.2, 137.6, 128.9, 127.8, 127.6, 63.1, 43.2, 38.8, 27.1. HRMS: calculated for $C_{14}H_{19}NO_3Na^+$ ($M+Na^+$): 272.1257, found: 272.1257.

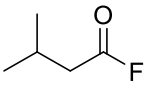


5-Chloropentanoyl fluoride (1u). Spectral data correlated with that previously reported in the literature.[29] *In situ* NMR data: ^{1}H NMR (500 MHz, CD_3CN) δ 3.61 (t, *J* = 6.3 Hz, 2H), 2.61 (t, *J* = 7.1 Hz, 2H), 1.87 – 1.79 (m, 2H), 1.79 – 1.72 (m,

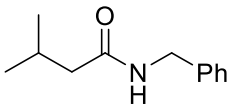
2H). ^{13}C NMR (126 MHz, CD_3CN) δ 163.8 (d, *J* = 358.6 Hz), 44.5, 31.0, 30.8 (d, *J* = 51.1 Hz), 21.0 (d, *J* = 2.9 Hz). ^{19}F NMR (377 MHz, CD_3CN) δ 42.92.



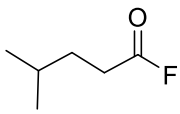
***N*-benzyl-5-chloropentanamide (5u).** 76% yield (34.1 mg, 0.15 mmol). Yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 2H), 7.30 – 7.26 (m, 3H), 5.81 (s, 1H), 4.43 (d, *J* = 5.7 Hz, 2H), 3.61 – 3.46 (m, 2H), 2.33 – 2.17 (m, 2H), 1.89 – 1.76 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.2, 138.3, 128.8, 127.8, 127.6, 44.6, 43.7, 35.7, 32.0, 23.0. HRMS: calculated for $C_{12}H_{17}ClNO^+$ ($M+H^+$): 226.09932, found: 226.09909.



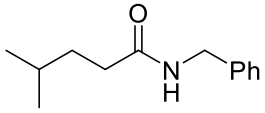
3-Methylbutanoyl fluoride (1v). Spectral data correlated with that previously reported in the literature.[20] *In situ* NMR data: ^{1}H NMR (500 MHz, CD_3CN) δ 2.46 (dd, *J* = 7.0, 2.2 Hz, 2H), 2.07 (ht, *J* = 6.8, 6.8 Hz, 1H), 0.99 (dd, *J* = 6.8, 1.0 Hz, 6H). ^{13}C NMR (126 MHz, CD_3CN) δ 163.2 (d, *J* = 360.1 Hz), 40.1 (d, *J* = 47.8 Hz), 24.8 (d, *J* = 1.8 Hz), 21.1. ^{19}F NMR (377 MHz, CD_3CN) δ 45.52.



***N*-benzyl-3-methylbutanamide (5v).** 78% yield (29.8 mg, 0.156 mmol). Spectral data correlated with that previously reported in the literature.[30] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 2H), 7.30 – 7.26 (m, 3H), 5.65 (s, 1H), 4.45 (d, *J* = 5.7 Hz, 2H), 2.16 (hd, *J* = 6.6, 1.4 Hz, 1H), 2.08 (d, *J* = 7.0 Hz, 2H), 0.97 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.2, 138.4, 128.7, 127.9, 127.5, 46.2, 43.6, 26.2, 22.5.

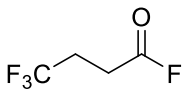


4-Methylpentanoyl fluoride (1w). *In situ* NMR data: ^{1}H NMR (500 MHz, CD_3CN) δ 2.57 (td, *J* = 7.6, 0.7 Hz, 2H), 1.61 (ht, *J* = 6.5, 6.5 Hz, 1H), 1.57 – 1.48 (m, 2H), 0.90 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (126 MHz, CD_3CN) δ 164.3 (d, *J* = 358.8 Hz), 32.3 (d, *J* = 2.2 Hz), 29.7 (d, *J* = 50.1 Hz), 27.1, 21.3. ^{19}F NMR (377 MHz, CD_3CN) δ 43.13.

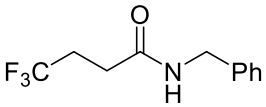


***N*-benzyl-4-methylpentanamide (5w).** 82% yield (33.7 mg, 0.16 mmol). Yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 2H), 7.31 – 7.26 (m, 3H), 5.72 (s, 1H), 4.44 (d, *J* = 5.7 Hz, 2H), 2.29 – 2.15 (m, 2H),

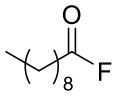
1.64 – 1.49 (m, 3H), 0.90 (d, *J* = 6.3 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.1, 138.4, 128.7, 127.9, 127.5, 43.6, 34.8, 34.6, 27.9, 22.3. HRMS: calculated for $C_{13}H_{19}NONa^+$ ($M+Na^+$): 228.1359, found: 228.1359.



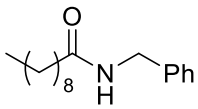
4,4,4-Trifluorobutanoyl fluoride (1x). *In situ* NMR data: ^{1}H NMR (800 MHz, CD_3CN) δ 2.88 (td, *J* = 7.5, 1.7 Hz, 2H), 2.57 (qt, *J* = 10.8, 3.5 Hz, 2H). ^{13}C NMR (201 MHz, CD_3CN) δ 162.6 (d, *J* = 355.7 Hz), 127.1 (q, *J* = 275.1 Hz), 28.6 (qd, *J* = 30.3, 3.8 Hz), 25.8 (dq, *J* = 58.6, 3.7 Hz). ^{19}F NMR (377 MHz, CD_3CN) δ 41.28 (q, *J* = 1.8 Hz), -67.63 (td, *J* = 10.7, 1.7 Hz).



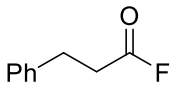
***N*-benzyl-4,4,4-trifluorobutanamide (5x).** 77% yield (35.7 mg, 0.15 mmol). Colorless solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (tt, *J* = 6.7, 1.2 Hz, 2H), 7.31 – 7.24 (m, 3H), 5.89 (s, 1H), 4.43 (d, *J* = 5.7 Hz, 2H), 2.61 – 2.39 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.5, 137.8, 128.8, 127.8, 127.7, 126.8 (q, *J* = 276.0 Hz), 43.9, 29.6 (q, *J* = 29.8 Hz), 28.8 (q, *J* = 3.0 Hz). HRMS: calculated for $C_{11}H_{12}F_3NONa^+$ ($M+Na^+$): 254.07632, found: 254.07649.



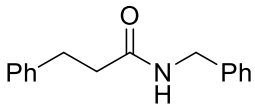
Decanoyl fluoride (1y). Spectral data correlated with that previously reported in the literature.[31] *In situ* NMR data: ^{1}H NMR (500 MHz, CD_3CN) δ 2.55 (t, *J* = 7.4 Hz, 2H), 1.61 (tt, *J* = 7.3, 7.3 Hz, 2H), 1.40 – 1.23 (m, 12H), 0.93 – 0.83 (m, 3H). ^{13}C NMR (126 MHz, CD_3CN) δ 164.1 (d, *J* = 359.3 Hz), 31.8, 31.6, 31.4, 29.1, 28.9, 28.8, 28.3, 23.6 (d, *J* = 2.4 Hz), 22.4, 13.4. ^{19}F NMR (377 MHz, CD_3CN) δ 43.06.



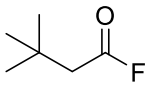
***N*-benzyldecanamide (5y).** 50% yield (25.9 mg, 0.10 mmol). Pale yellow solid. Spectral data correlated with that previously reported in the literature.[32] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 2H), 7.31 – 7.26 (m, 3H), 5.68 (s, 1H), 4.45 (d, *J* = 5.7 Hz, 2H), 2.25 – 2.11 (m, 2H), 1.66 (tt, *J* = 7.5, 7.5 Hz, 2H), 1.36 – 1.22 (m, 12H), 0.88 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.0, 138.4, 128.7, 127.9, 127.5, 43.6, 36.9, 31.9, 29.5, 29.4, 29.3, 29.3, 25.8, 22.7, 14.1.



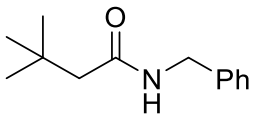
3-Phenylpropanoyl fluoride (1z). Spectral data correlated with that previously reported in the literature.[33] *In situ* NMR data: ^{1}H NMR (500 MHz, CD_3CN) δ 7.36 – 7.29 (m, 2H), 7.28 – 7.19 (m, 3H), 2.99 – 2.93 (m, 2H), 2.92 – 2.87 (m, 2H). ^{13}C NMR (126 MHz, CD3CN) δ 164.3 (d, J = 359.4 Hz), 140.6, 129.5, 129.2, 127.5, 34.2 (d, J = 50.4 Hz), 30.4, 30.3. ^{19}F NMR (377 MHz, CD_3CN) δ 43.84.



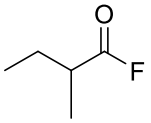
***N*-benzyl-3-phenylpropanamide (5z).** 92% yield (44.0 mg, 0.18 mmol). Pale yellow solid. Spectral data correlated with that previously reported in the literature.[34] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.25 (m, 5H), 7.24 – 7.18 (m, 3H), 7.17 – 7.11 (m, 2H), 5.65 (s, 1H), 4.40 (d, *J* = 5.7 Hz, 2H), 3.00 (t, *J* = 7.6 Hz, 2H), 2.52 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.8, 140.8, 138.2, 128.7, 128.6, 128.4, 127.8, 127.5, 126.3, 43.6, 38.5, 31.7.



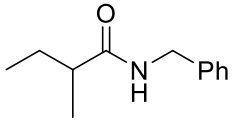
3,3-Dimethylbutanoyl fluoride (1aa). Spectral data correlated with that previously reported in the literature.[20] *In situ* NMR data: ^{1}H NMR (500 MHz, CD_3CN) δ 2.46 (d, *J* = 4.7 Hz, 2H), 1.06 (d, *J* = 1.0 Hz, 9H). ^{13}C NMR (126 MHz, CD_3CN) δ 162.2 (d, *J* = 361.2 Hz), 44.9 (d, *J* = 46.6 Hz), 28.3 (d, *J* = 2.3 Hz), 27.8. ^{19}F NMR (377 MHz, CD_3CN) δ 52.54.



***N*-benzyl-3,3-dimethylbutanamide (5aa).** 77% yield (31.6 mg, 0.15 mmol). Colorless solid. Spectral data correlated with that previously reported in the literature.[35] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 2H), 7.31 – 7.27 (m, 3H), 5.61 (s, 1H), 4.44 (d, *J* = 5.7 Hz, 2H), 2.09 (s, 2H), 1.05 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.5, 138.5, 128.7, 127.9, 127.5, 50.7, 43.6, 31.0, 29.9.

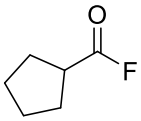


2-Methylbutanoyl fluoride (1bb). *In situ* NMR data: ^{1}H NMR (500 MHz, CD_3CN) δ 1.83 – 1.64 (m, 2H), 1.63 – 1.59 (m, 1H), 1.22 (d, *J* = 0.6 Hz, 3H), 0.95 (td, *J* = 7.5, 1.0 Hz, 3H). ^{13}C NMR (126 MHz, CD_3CN) δ 166.4 (d, *J* = 366.9 Hz), 39.2 (d, *J* = 46.4 Hz), 25.4, 14.7, 10.4. ^{19}F NMR (471 MHz, CD_3CN) δ 35.98.

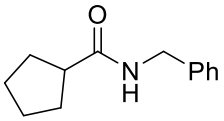


***N*-benzyl-2-methylbutanamide (5bb).** 51% yield (19.5 mg, 0.10 mmol). Colorless solid. Spectral data correlated with that previously reported in the literature.[36] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 2H), 7.30 – 7.26

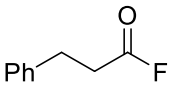
(m, 3H), 5.74 (s, 1H), 4.45 (ddd, *J* = 21.2, 9.0, 6.1 Hz, 2H), 2.13 (tq, *J* = 6.9, 6.8 Hz, 1H), 1.76 – 1.65 (m, 1H), 1.45 (dqd, *J* = 13.6, 7.4, 6.2 Hz, 1H), 1.16 (d, *J* = 6.9 Hz, 3H), 0.91 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.3, 138.6, 128.7, 127.8, 127.5, 43.5, 43.3, 27.4, 17.6, 12.0.



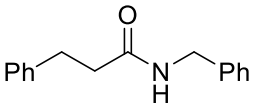
Cyclopentanecarbonyl fluoride (1cc). *In situ* NMR data: ^{1}H NMR (800 MHz, CD_3CN) δ 2.30 (t, *J* = 7.5 Hz, 1H), 2.10 – 2.05 (m, 1H), 2.00 – 2.05 (m, 1H), 2.00 – 1.94 (m, 1H), 1.86 – 1.75 (m, 3H), 1.66 – 1.56 (m, 2H). ^{13}C NMR (201 MHz, CD_3CN) δ 167.2 (d, *J* = 361.5 Hz), 42.3 (d, *J* = 48.3 Hz), 32.6, 26.3 (d, *J* = 103.0 Hz). ^{19}F NMR (471 MHz, CD_3CN) δ 37.35.



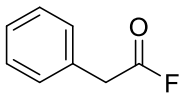
***N*-benzylcyclopentanecarboxamide (5cc).** 54% yield (22.0 mg, 0.108 mmol). Spectral data correlated with that previously reported in the literature.[37] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 2H), 7.30 – 7.26 (m, 3H), 5.70 (s, 1H), 4.45 (d, *J* = 5.7 Hz, 2H), 2.54 (p, *J* = 8.1 Hz, 1H), 1.95 – 1.66 (m, 6H), 1.66 – 1.51 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.0, 138.6, 128.7, 127.8, 127.5, 45.9, 43.6, 30.5, 26.0.



3-Phenylpropanoyl fluoride (1dd). Spectra data is the same as **1z.** Spectra data matches with literature.[33] *In situ* NMR data: ^{1}H NMR (500 MHz, CD_3CN) δ 7.36 – 7.29 (m, 2H), 7.28 – 7.19 (m, 3H), 2.99 – 2.93 (m, 2H), 2.92 – 2.87 (m, 2H). ^{13}C NMR (126 MHz, CD_3CN) δ 164.3 (d, J = 359.4 Hz), 140.6, 129.5, 129.2, 127.5, 34.2 (d, J = 50.4 Hz), 30.4, 30.3. ^{19}F NMR (377 MHz, CD_3CN) δ 43.84.

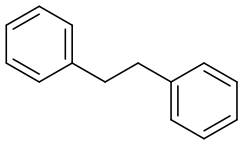


***N*-benzyl-3-phenylpropanamide (5dd).** 75% yield (36.0 mg, 0.15 mmol). Pale yellow solid. Spectral data correlated with that previously reported in the literature.[34] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.25 (m, 5H), 7.24 – 7.18 (m, 3H), 7.17 – 7.11 (m, 2H), 5.65 (s, 1H), 4.40 (d, *J* = 5.7 Hz, 2H), 3.00 (t, *J* = 7.6 Hz, 2H), 2.52 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.8, 140.8, 138.1, 128.7, 128.6, 128.4, 127.8, 127.5, 126.3, 43.6, 38.6, 31.7.

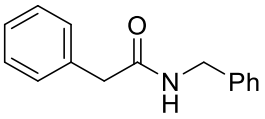


2-Phenylacetyl fluoride (1ee). Spectral data correlated with that previously reported in the literature.[16] *In situ* NMR data: ^{1}H NMR (400 MHz, CD_3CN) δ 7.43 –7.31 (m, 5H), 3.92 (s, 2H). ^{13}C NMR (126 MHz, CD_3CN) δ 163.4 (d, *J* = 359.8 Hz), 130.5 (d, *J*

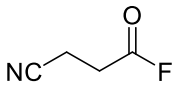
= 1.3 Hz), 129.7 (two signals overlapped), 128.7, 39.0 (d, *J* = 55.2 Hz). ^{19}F NMR (377 MHz, CD_3CN) δ 41.90.



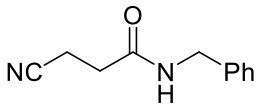
1,2-Diphenylethane. Spectral data correlated with that previously reported in the literature.[38] ^{1}H NMR (500 MHz, CD_3CN) δ 7.30 – 7.25 (m, 2H), 7.24 – 7.20 (m, 2H), 7.20 – 7.15 (m, 1H), 2.91 (s, 2H). ^{13}C NMR (126 MHz, CD_3CN) δ 142.9, 129.4, 129.2, 126.8, 38.3



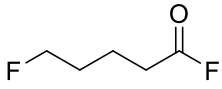
***N*-benzyl-2-phenylacetamide (5ee).** 64% yield (29.0 mg, 0.13 mmol). Yellow solid. Spectral data correlated with that previously reported in the literature.[39] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.32 (m, 2H), 7.32 – 7.22 (m, 6H), 7.20 – 7.15 (m, 2H), 5.76 (s, 1H), 4.41 (d, *J* = 5.8 Hz, 2H), 3.62 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.9, 138.2, 134.8, 129.5, 129.1, 128.7, 127.5, 127.4, 127.4, 43.9, 43.6.



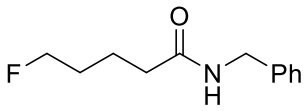
3-Cyanopropanoyl fluoride (1ff). *In situ* NMR data: ^{1}H NMR (500 MHz, CD_3CN) δ 2.95 (td, *J* = 6.8, 2.8 Hz, 2H), 2.70 (t, *J* = 6.9 Hz, 2H). ^{13}C NMR (126 MHz, CD_3CN) δ 162.0 (d, *J* = 356.6 Hz), 118.3, 28.1 (d, *J* = 58.1 Hz), 12.1 (d, *J* = 4.6 Hz). ^{19}F NMR (377 MHz, CD_3CN) δ 40.68.



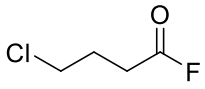
***N*-benzyl-3-cyanopropanamide (5ff).** 85% yield (31.9 mg, 0.17 mmol). Pale yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 2H), 7.31 – 7.26 (m, 3H), 5.93 (s, 1H), 4.45 (d, *J* = 5.7 Hz, 2H) 2.70 (t, *J* = 7.1 Hz, 2H), 2.55 (t, *J* = 7.3 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.5, 137.6, 128.9, 127.9, 127.8, 119.0, 44.0, 31.6, 13.2. HRMS: calculated for $C_{11}H_{12}N_2ONa^+$ ($M+Na^+$): 211.0842, found: 211.0833.



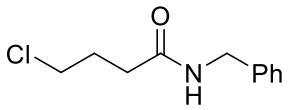
5-Fluoropentanoyl fluoride (1gg). *In situ* NMR data: ^{1}H NMR (500 MHz, CD_3CN) δ 4.53 – 4.49 (m, 1H), 4.43 – 4.40 (m, 1H), 2.65 – 2.59 (m, 2H), 1.77 – 1.68 (m, 4H). ^{13}C NMR (126 MHz, CD_3CN) δ 163.9 (d, *J* = 358.8 Hz), 83.6 (d, *J* = 161.8 Hz), 31.1 (d, *J* = 50.8 Hz), 28.9 (d, *J* = 19.6 Hz), 19.7 (dd, *J* = 5.4, 3.0 Hz). ^{19}F NMR (377 MHz, CD_3CN) δ 42.86, -219.75.



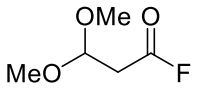
***N*-benzyl-5-fluoropentanamide (5gg).** 76% yield (31.9 mg, 0.15 mmol). Yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 2H), 7.30 – 7.26 (m, 3H), 5.81 (s, 1H), 4.50 (t, *J* = 5.6 Hz, 1H), 4.43 (d, *J* = 5.7 Hz, 2H), 4.41 (t, *J* = 5.8 Hz, 1H), 2.27 (t, *J* = 7.2 Hz, 2H), 1.87 – 1.64 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.3, 138.3, 128.8, 127.8, 127.6, 83.9 (d, *J* = 164.5 Hz), 43.6, 36.0, 29.8 (d, *J* = 19.6 Hz), 21.7 (d, *J* = 5.0 Hz). HRMS: calculated for $C_{12}H_{16}FNONa^+$ ($M+Na^+$): 232.1108, found: 232.1100.



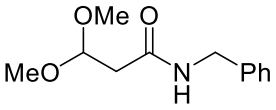
4-Chlorobutanoyl fluoride (1hh). Spectral data correlated with that previously reported in the literature.[40] *In situ* NMR data: ^{1}H NMR (500 MHz, CD_3CN) δ 3.65 (td, *J* = 6.4, 1.2 Hz, 2H), 2.74 (td, *J* = 7.3, 0.7 Hz, 2H), 2.14 – 2.05 (m, 2H). ^{13}C NMR (126 MHz, CD_3CN) δ 163.5 (d, *J* = 357.9 Hz), 43.6, 29.1 (d, *J* = 52.7 Hz), 26.6 (d, *J* = 3.3 Hz). ^{19}F NMR (377 MHz, CD_3CN) δ 43.00.



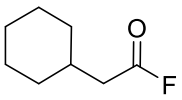
***N*-benzyl-4-chlorobutanamide (5hh).** 89% yield (32.2 mg, 0.15 mmol). Pale yellow solid. Spectral data correlated with that previously reported in the literature.[41] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 2H), 7.31 – 7.23 (m, 3H), 5.93 (s, 1H), 4.43 (d, *J* = 5.7 Hz, 2H), 3.60 (t, *J* = 6.2 Hz, 2H), 2.39 (t, *J* = 7.1 Hz, 2H), 2.13 (tt, *J* = 6.9, 6.0 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.5, 138.2, 128.8, 127.8, 127.6, 44.5, 43.7, 33.2, 28.1.



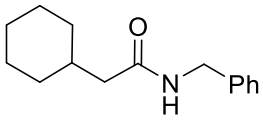
3,3-Dimethoxypropanoyl fluoride (1ii). *In situ* NMR data: ^{1}H NMR (500 MHz, CD_3CN) δ 4.77 (t, *J* = 5.7 Hz, 1H), 3.35 (s, 6H), 2.88 (dd, *J* = 5.7, 2.9 Hz, 2H). ^{13}C NMR (126 MHz, CD_3CN) δ 160.2 (d, J = 357.5 Hz), 100.2 (d, J = 3.2 Hz), 53.5, 37.1 (d, J = 50.4 Hz).^{19}F NMR (377 MHz, CD_3CN) δ 46.29.



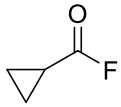
***N*-benzyl-3,3-dimethoxypropanamide (5ii).** 74% yield (32.9 mg, 0.15 mmol). Pale yellow solid. Spectral data correlated with that previously reported in the literature.[42]^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 2H), 7.25-7.28 (m, 3H), 6.40 (s, 1H), 4.72 (t, *J* = 5.3 Hz, 1H), 4.46 (d, *J* = 5.8 Hz, 2H), 3.38 (s, 6H), 2.59 (d, *J* = 5.3 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.9, 138.3, 128.7, 127.6, 127.4, 102.2, 54.2, 43.4, 41.0.



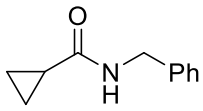
2-Cyclohexylacetyl fluoride (1jj). *In situ* NMR data: ^{1}H NMR (500 MHz, CD_3CN) δ 2.45 (dd, *J* = 6.6, 2.6 Hz, 2H), 1.83 – 1.66 (m, 5H), 1.69 – 1.59 (m, 1H), 1.38 – 1.23 (m, 2H), 1.18 (tt, *J* = 12.4, 3.2 Hz, 1H), 1.03 (tt, *J* = 14.0, 6.9 Hz, 2H). ^{13}C NMR (126 MHz, CD_3CN) δ 163.1 (d, *J* = 359.9 Hz), 39.0 (d, *J* = 47.9 Hz), 33.9 (d, *J* = 1.4 Hz), 32.2, 25.7, 25.6. ^{19}F NMR (377 MHz, CD_3CN) δ 45.76.



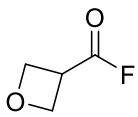
***N*-benzyl-2-cyclohexylacetamide (5jj).** 67% yield (31.0 mg, 0.13 mmol). Colorless solid. Spectral data correlated with that previously reported in the literature.[43] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 2H), 7.30 – 7.25 (m, 3H), 5.76 (s, 1H), 4.43 (d, *J* = 5.6 Hz, 2H), 2.07 (d, *J* = 7.1 Hz, 2H), 1.83 (dddt, *J* = 14.5, 10.9, 7.3, 3.5 Hz, 1H), 1.78 – 1.60 (m, 5H), 1.27 (dddd, *J* = 25.6, 12.3, 3.3, 3.0 Hz, 2H), 1.13 (dddd, *J* = 25.3, 12.5, 3.5, 3.3 Hz, 2H), 0.94 (ddd, *J* = 24.2, 12.5, 3.2 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.2, 138.5, 128.7, 127.8, 127.5, 44.9, 43.6, 35.4, 33.2, 26.2, 26.1.



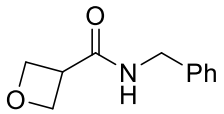
Cyclopropanecarbonyl fluoride (1kk). Spectral data correlated with that previously reported in the literature.[20] *In situ* NMR data: ^{1}H NMR (500 MHz, CD_3CN) δ 1.71 (ddd, *J* = 12.4, 6.4, 6.1 Hz, 1H), 1.14 (d, *J* = 6.1 Hz, 4H). ^{13}C NMR (126 MHz, CD_3CN) δ 165.4 (d, *J* = 343.7 Hz), 10.3 (d, *J* = 73.5 Hz), 9.6. ^{19}F NMR (471 MHz, CD_3CN) δ 31.15.



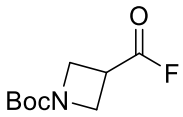
***N*-benzylcyclopropanecarboxamide (5kk).** 57% yield (20.1 mg, 0.11 mmol). Colorless solid. Spectral data correlated with that previously reported in the literature.[44] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.32 (m, 2H), 7.32 – 7.26 (m, 3H), 5.92 (s, 1H), 4.46 (d, *J* = 5.6 Hz, 2H), 1.35 (tt, *J* = 7.9, 4.6 Hz, 1H), 1.04 – 0.99 (m, 2H), 0.79 – 0.71 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.4, 138.5, 128.7, 127.9, 127.5, 43.9, 14.8, 7.2.



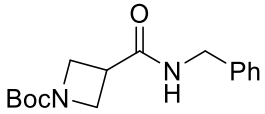
Oxetane-3-carbonyl fluoride (1ll). *In situ* NMR data: ^{1}H NMR (500 MHz, CD_3CN) δ 4.82 (ddd, *J* = 8.7, 6.4, 0.9 Hz, 2H), 4.74 (ddd, *J* = 6.4, 6.4, 0.8 Hz, 2H), 4.07 (tt, *J* = 8.7, 6.3 Hz, 1H). ^{13}C NMR (126 MHz, CD_3CN) δ 163.06 (d, *J* = 357.5 Hz), 71.6, 37.22 (d, *J* = 56.7 Hz). ^{19}F NMR (377 MHz, CD_3CN) δ 35.54.



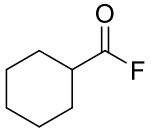
***N*-benzyloxetane-3-carboxamide (5ll).** 92% yield (35.0 mg, 0.18 mmol). Pale yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.31 (m, 2H), 7.30 – 7.24 (m, 3H), 6.13 – 5.96 (m, 1H), 4.86 (dd, *J* = 6.4, 6.2 Hz, 2H), 4.76 (dd, *J* = 8.4, 6.0 Hz, 2H), 4.45 (d, *J* = 5.7 Hz, 2H), 3.70 (tt, *J* = 8.4, 6.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.2, 137.9, 128.8, 127.9, 127.7, 73.4, 43.8, 40.25. HRMS: calculated for $C_{11}H_{13}NO_2Na^+$ ($M+Na^+$): 214.0838, found: 214.0836.



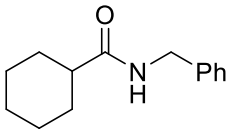
Tert-butyl 3-(fluorocarbonyl)azetidine-1-carboxylate (1mm). *In situ* NMR data: ^{1}H NMR (500 MHz, CD_3CN) δ 4.11 (dd, *J* = 8.9, 8.8 Hz, 2H), 4.03 (dd, *J* = 8.7, 5.7 Hz, 2H), 3.61 (tt, *J* = 9.1, 5.8 Hz, 1H), 1.41 (s, 9H). ^{13}C NMR (126 MHz, CD_3CN) δ 163.2 (d, *J* = 357.2 Hz), 155.9, 79.4, 50.9, 30.7 (d, *J* = 58.7 Hz), 27.4. ^{19}F NMR (471 MHz, CD_3CN) δ 35.61.



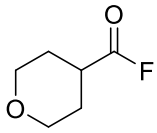
Tert-butyl 3-(benzylcarbamoyl)azetidine-1-carboxylate (5mm). 69% yield (40.2 mg, 0.14 mmol). Yellow oil. Spectral data correlated with that previously reported in the literature.[45] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 2H), 7.31 – 7.25 (m, 3H), 5.90 (s, 1H), 4.45 (d, *J* = 5.7 Hz, 2H), 4.15 – 4.09 (m, 2H), 4.04 (dd, *J* = 8.6, 8.5 Hz, 2H), 3.18 (tt, *J* = 8.7, 6.1 Hz, 1H), 1.43 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.4, 156.2, 137.8, 128.8, 127.9, 127.8, 79.8, 51.8 (br), 43.9, 33.4, 28.4.



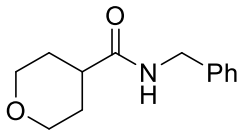
Cyclohexanecarbonyl fluoride (1nn). Spectral data correlated with that previously reported in the literature.[46] *In situ* NMR data: ^{1}H NMR (500 MHz, CD_3CN) δ 2.61 (tt, *J* = 10.8, 3.8 Hz, 1H), 2.00 – 1.95 (m, 2H), 1.77 – 1.69 (m, 2H), 1.67 – 1.58 (m, 1H), 1.54 – 1.45 (m, 2H), 1.39 – 1.22 (m, 3H). ^{13}C NMR (126 MHz, CD_3CN) δ 165.8 (d, J = 365.5 Hz), 40.9 (d, J = 46.4 Hz), 27.7, 25.1, 24.8. ^{19}F NMR (471 MHz, CD_3CN) δ 34.54.



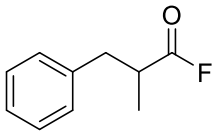
***N*-benzylcyclohexanecarboxamide (5nn).** 79% yield (34.2 mg, 0.16 mmol). Colorless solid. Spectral data correlated with that previously reported in the literature.[47] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 2H), 7.31 – 7.25 (m, 3H), 5.78 (s, 1H), 4.44 (d, *J* = 5.7 Hz, 2H), 2.12 (tt, *J* = 11.8, 3.5 Hz, 1H), 1.94 – 1.84 (m, 2H), 1.78-1.83 (m, 2H), 1.65-1.70 (m, 1H), 1.47 (ddd, *J* = 12.3, 11.9, 3.3 Hz, 2H), 1.36 – 1.16 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.9, 138.8, 128.7, 127.7, 127.4, 45.6, 43.4, 29.8, 25.8.



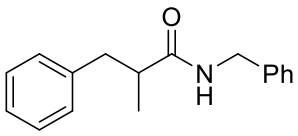
Tetrahydro-2H-pyran-4-carbonyl fluoride (1oo). *In situ* NMR data: ^{1}H NMR (500 MHz, CD_3CN) δ 3.93 – 3.85 (m, 2H), 3.41 (ddd, *J* = 11.8, 11.0, 2.4 Hz, 2H), 2.87 (ttd, *J* = 11.0, 4.1, 1.6 Hz, 1H), 1.91 – 1.85 (m, 2H), 1.79 – 1.67 (m, 2H). ^{13}C NMR (126 MHz, CD_3CN) δ 164.7 (d, *J* = 364.4 Hz), 66.0, 38.2 (d, *J* = 49.5 Hz), 27.5. ^{19}F NMR (471 MHz, CD_3CN) δ 33.74.



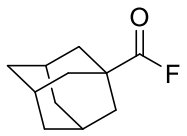
***N*-benzyltetrahydro-2H-pyran-4-carboxamide (5oo).** 83% yield (36.5 mg, 0.17 mmol). Yellow solid. Spectral data correlated with that previously reported in the literature.[48] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 2H), 7.30 – 7.24 (m, 3H), 5.78 (s, 1H), 4.45 (d, *J* = 5.6 Hz, 2H), 4.01 (ddd, *J* = 11.6, 4.4, 2.2 Hz, 2H), 3.40 (ddd, *J* = 11.5, 8.8, 2.7 Hz, 2H), 2.36 (tt, *J* = 11.3, 4.3 Hz, 1H), 1.90 – 1.74 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.0, 138.2, 128.8, 127.8, 127.6, 67.3, 43.6, 42.3, 29.3.



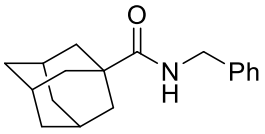
2-Methyl-3-phenylpropanoyl fluoride (1pp). *In situ* NMR data: ^{1}H NMR (500 MHz, CD_3CN) δ 7.37 – 7.28 (m, 3H), 7.27 – 7.22 (m, 2H), 3.07 – 2.96 (m, 2H), 2.87 – 2.79 (m, 1H), 1.20 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (126 MHz, CD_3CN) δ 165.8 (d, *J* = 366.7 Hz), 138.2, 129.0, 128.5, 126.7, 39.9 (d, *J* = 46.8 Hz), 38.0, 14.9. ^{19}F NMR (377 MHz, CD_3CN) δ 36.47.



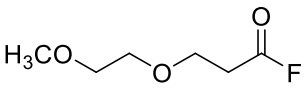
***N*-benzyl-2-methyl-3-phenylpropanamide (5pp).** 67% yield (33.9 mg, 0.13 mmol). Pale yellow solid. Spectral data correlated with that previously reported in the literature.[49] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.20 (m, 6H), 7.19 – 7.13 (m, 2H), 7.03 (dd, *J* = 7.6, 1.9 Hz, 2H), 5.50 (s, 1H), 4.39 (dd, *J* = 14.8, 6.0 Hz, 1H), 4.28 (dd, *J* = 14.8, 5.4 Hz, 1H), 2.99 (dd, *J* = 13.4, 8.7 Hz, 1H), 2.71 (dd, *J* = 13.4, 6.2 Hz, 1H), 2.47 (dtd, *J* = 8.7, 6.7, 2.0 Hz, 1H), 1.23 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.3, 139.9, 138.2, 129.0, 128.6, 128.5, 127.7, 127.4, 126.3, 44.1, 43.4, 40.6, 17.9.



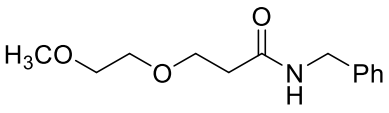
(3r,5r,7r)-Adamantane-1-carbonyl fluoride (1qq). Spectral data correlated with that previously reported in the literature.[16] *In situ* NMR data: ^{1}H NMR (500 MHz, CD_3CN) δ 2.06 – 2.00 (m, 3H), 1.97 (t, J = 1.9 Hz, 6H), 1.81 – 1.69 (m, 6H). ^{13}C NMR (126 MHz, CD_3CN) δ 167.01 (d, J = 370.8 Hz), 40.46 (d, J = 44.7 Hz), 37.46, 35.62, 27.38. ^{19}F NMR (471 MHz, CD3CN) δ 21.87.



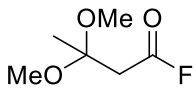
(3r,5r,7r)-*N*-benzyladamantane-1-carboxamide (5qq). 99% yield (54.0 mg, 0.20 mmol). Colorless solid. Spectral data correlated with that previously reported in the literature.[50] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 2H), 7.29 – 7.21 (m, 3H), 5.90 (s, 1H), 4.43 (d, *J* = 5.6 Hz, 2H), 2.04 (s, 3H), 1.88 (d, *J* = 3.0 Hz, 6H), 1.77 – 1.64 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.8, 138.7, 128.7, 127.6, 127.4, 43.3, 40.7, 39.3, 36.5, 28.2.



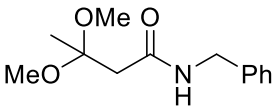
3-(2-Methoxyethoxy)propanoyl fluoride (1rr). *In situ* NMR data: ^{1}H NMR (500 MHz, CD_3CN) δ 3.71 (td, *J* = 6.0, 1.0 Hz, 2H), 3.59 – 3.54 (m, 2H), 3.48 – 3.43 (m, 2H), 3.29 (s, 3H), 2.80 (td, *J* = 6.0, 1.7 Hz, 2H). ^{13}C NMR (126 MHz, CD_3CN) δ 162.2 (d, *J* = 358.6 Hz), 71.5, 70.1, 65.0 (d, *J* = 2.7 Hz), 57.9, 33.2 (d, *J* = 51.7 Hz). ^{19}F NMR (377 MHz, CD_3CN) δ 43.38.



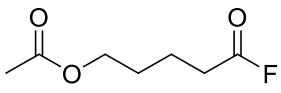
***N*-benzyl-3-(2-methoxyethoxy)propenamide (5rr).** 53% yield (25.0 mg, 0.10 mmol). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.23 (m, 5H), 6.84 (s, 1H), 4.45 (d, *J* = 5.8 Hz, 2H), 3.76 (dd, *J* = 6.0, 5.3 Hz, 2H), 3.66 – 3.59 (m, 2H), 3.51 – 3.44 (m, 2H), 3.24 (s, 3H), 2.54 (t, *J* = 5.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.5, 138.6, 128.6, 127.6, 127.3, 71.5, 70.1, 67.2, 58.9, 43.4, 36.9. HRMS: calculated for $C_{13}H_{19}NO_3Na^+$ ($M+Na^+$): 260.1257, found: 260.1255.



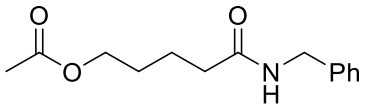
3,3-Dimethoxybutanoyl fluoride (1ss). *In situ* NMR data: ^{1}H NMR (500 MHz, CD_3CN) δ 3.18 (s, 6H), 2.91 (dd, *J* = 4.9, 0.7 Hz, 2H), 1.44 (d, *J* = 0.6 Hz, 3H). ^{13}C NMR (126 MHz, CD_3CN) δ 160.0 (d, *J* = 357.5 Hz), 99.03 (d, *J* = 3.1 Hz), 48.0, 40.1 (d, *J* = 50.7 Hz), 21.1 (d, *J* = 1.9 Hz). ^{19}F NMR (377 MHz, CD_3CN) δ 51.33.



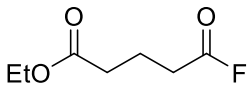
***N*-benzyl-3,3-dimethoxybutanamide (5ss).** 66% yield (31.2 mg, 0.13 mmol). Pale yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 2H), 7.29 – 7.25 (m, 3H), 6.81 (s, 1H), 4.45 (d, *J* = 5.8 Hz, 2H), 3.20 (s, 6H), 2.64 (s, 2H), 1.39 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.5, 138.6, 128.7, 127.6, 127.4, 99.9, 48.5, 44.7, 43.4, 21.2. HRMS: calculated for $C_{13}H_{19}NO_3Na^+$ ($M+Na^+$): 260.1257, found: 260.1261.



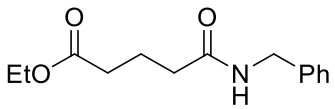
5-Fluoro-5-oxopentyl acetate (1tt). *In situ* NMR data: ^{1}H NMR (500 MHz, CD_3CN) δ 4.03 (tt, *J* = 6.2, 1.9 Hz, 2H), 2.66 – 2.56 (m, 2H), 1.99 (s, 3H), 1.70 – 1.65 (m, 4H). ^{13}C NMR (126 MHz, CD_3CN) δ 170.7, 163.9 (d, *J* = 358.7 Hz), 63.4, 31.1 (d, *J* = 50.5 Hz), 27.2, 20.3 (d, *J* = 2.8 Hz), 20.1. ^{19}F NMR (377 MHz, CD_3CN) δ 42.93.



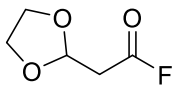
5-(Benzylamino)-5-oxopentyl acetate (5tt). 71% yield (35.3 mg, 0.14 mmol). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 2H), 7.31 – 7.26 (m, 3H), 5.74 (s, 1H), 4.44 (d, *J* = 5.6 Hz, 2H), 4.07 (t, *J* = 6.3 Hz, 2H), 2.24 (t, *J* = 7.3 Hz, 2H), 2.03 (s, 3H), 1.79 – 1.71 (m, 2H), 1.71 – 1.64 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.2, 171.2, 138.3, 128.8, 127.9, 127.6, 64.0, 43.7, 36.1, 28.2, 22.1, 21.0. HRMS: calculated for $C_{14}H_{19}NO_3Na^+$ ($M+Na^+$): 272.1257, found: 272.1263.



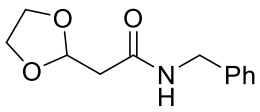
Ethyl 5-fluoro-5-oxopentanoate (1uu). *In situ* NMR data: ^{1}H NMR (500 MHz, CD_3CN) δ 4.09 (q, *J* = 7.1 Hz, 2H), 2.63 (t, *J* = 7.3 Hz, 2H), 2.37 (td, *J* = 7.4, 1.0 Hz, 2H), 1.89 (tt, *J* = 7.3, 7.3 Hz, 2H), 1.21 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, CD_3CN) δ 173.4, 164.7 (d, *J* = 358.5 Hz), 61.1, 33.2, 31.6 (d, *J* = 51.4 Hz), 20.0 (d, *J* = 3.2 Hz), 14.5. ^{19}F NMR (471 MHz, CD_3CN) δ 42.84.



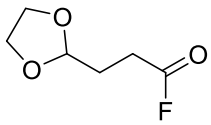
Ethyl 5-(benzylamino)-5-oxopentanoate (5uu). 86% yield (42.7 mg, 0.17 mmol). Yellow liquid. Spectral data correlated with that previously reported in the literature.[51] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 2H), 7.29 – 7.23 (m, 3H), 5.90 (s, 1H), 4.43 (d, *J* = 5.7 Hz, 2H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.36 (t, *J* = 7.2 Hz, 2H), 2.27 (t, *J* = 7.4 Hz, 2H), 1.98 (tt, *J* = 7.2, 7.1 Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.2, 172.0, 138.3, 128.7, 127.8, 127.5, 60.4, 43.6 35.5, 33.4, 21.0, 14.2.



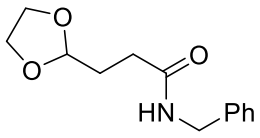
2-(1,3-Dioxolan-2-yl)acetyl fluoride (1vv). *In situ* NMR data: ^{1}H NMR (500 MHz, CD_3CN) δ 5.24 (td, *J* = 4.9, 1.2 Hz, 1H), 3.99 – 3.92 (m, 2H), 3.90 – 3.84 (m, 2H), 2.92 (dd, *J* = 4.8, 2.3 Hz, 2H). ^{13}C NMR (126 MHz, CD_3CN) δ 159.8 (d, *J* = 358.0 Hz), 99.4 (d, *J* = 3.3 Hz), 65.0, 37.7 (d, *J* = 49.6 Hz). ^{19}F NMR (377 MHz, CD_3CN) δ 47.78.



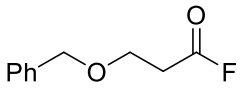
***N*-benzyl-2-(1,3-dioxolan-2-yl)acetamide (5vv).** 39% yield (17.3 mg, 0.08 mmol). Yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.31 (m, 2H), 7.30 – 7.26 (m, 3H), 6.44 (s, 1H), 5.17 (t, *J* = 4.6 Hz, 1H), 4.46 (d, *J* = 5.7 Hz, 2H), 3.98 – 3.92 (m, 2H), 3.92 – 3.86 (m, 2H), 2.67 (d, *J* = 4.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.2, 138.3, 128.7, 127.7, 127.4, 101.1, 65.0, 43.5, 41.5. HRMS: calculated for $C_{12}H_{15}NO_3Na^+$ ($M+Na^+$): 244.0944, found: 244.0944.



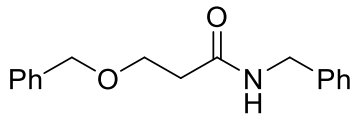
3-(1,3-Dioxan-2-yl)propanoyl fluoride (1ww). *In situ* NMR data: ^{1}H NMR (500 MHz, CD_3CN) δ 4.92 (td, *J* = 3.9, 0.9 Hz, 1H), 3.92 – 3.89 (m, 2H), 3.84 – 3.81 (m, 2H), 2.62 (td, *J* = 7.2, 1.2 Hz, 2H), 1.99 (td, *J* = 7.2, 3.9 Hz, 2H). ^{13}C NMR (126 MHz, CD_3CN) δ 163.8 (d, *J* = 357.6 Hz), 102.0, 37.1, 27.7(d, *J* = 2.1 Hz), 26.0 (d, *J* = 54.3 Hz). ^{19}F NMR (377 MHz, CD_3CN) δ 41.62.



***N*-benzyl-3-(1,3-dioxolan-2-yl)propanamide (5ww).** 62% yield (30.9 mg, 0.12 mmol). Yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 2H), 7.29 – 7.24 (m, 3H), 5.96 (s, 1H), 4.92 (t, *J* = 4.3 Hz, 1H), 4.42 (d, *J* = 5.7 Hz, 2H), 3.97 – 3.88 (m, 2H), 3.88 – 3.78 (m, 2H), 2.35 (t, *J* = 7.4 Hz, 2H), 2.04 (td, *J* = 7.4, 4.9 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.2, 138.4, 128.7, 127.8, 127.5, 103.4, 65.0, 43.6, 30.6, 29.3.

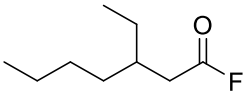


3-(Benzyloxy)propanoyl fluoride (1xx). *In situ* NMR data: ^{1}H NMR (800 MHz, CD_3CN) δ 7.38 – 7.29 (m, 5H), 4.52 (s, 2H), 3.73 (td, *J* = 5.9, 0.9 Hz, 2H), 2.84 (td, *J* = 5.9, 1.6 Hz, 2H). ^{13}C NMR (201 MHz, CD_3CN) δ 162.8 (d, *J* = 358.8 Hz), 138.8, 128.9, 128.3, 128.2 (d, *J* = 2.2 Hz), 73.2, 64.8 (d, *J* = 2.2 Hz), 33.7 (d, *J* = 52.1 Hz). ^{19}F NMR (377 MHz, CD_3CN) δ 43.39.

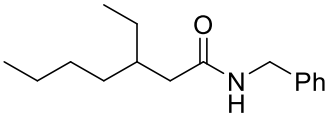


***N*-benzyl-3-(benzyloxy)propanamide (5xx).** 48% yield (26.0 mg, 0.10 mmol). Yellow solid. Spectral data correlated with that previously reported in the literature.[52] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.25 (m, 8H), 7.24 – 7.19 (m, 2H), 6.52 (s, 1H), 4.51 (s, 2H), 4.44 (d, *J* = 5.7 Hz, 2H), 3.77 (t, *J* = 5.7 Hz, 2H), 2.55 (t, *J* = 5.7 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.3, 138.3,

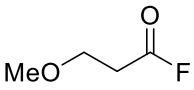
137.6, 128.7, 128.5, 127.9, 127.8, 127.7, 127.4, 73.4, 66.4, 43.5, 37.2. HRMS: calculated for $C_{17}H_{19}NO_2Na^+$ ($M+Na^+$): 292.13080, found: 292.13060.



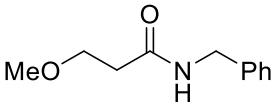
3-Ethylheptanoyl fluoride (1yy). *In situ* NMR data: ^{1}H NMR (500 MHz, CD_3CN) δ 2.51 (dd, *J* = 6.7, 2.7 Hz, 2H), 2.07 – 1.99 (m, 1H), 1.42 – 1.23 (m, 8H), 0.95 – 0.84 (m, 6H). ^{13}C NMR (126 MHz, CD_3CN) δ 163.6 (d, *J* = 360.0 Hz), 36.2, 35.6 (d, *J* = 1.6 Hz), 32.4, 28.4, 25.8, 22.5, 13.3, 10.0. ^{19}F NMR (377 MHz, CD_3CN) δ 46.38.



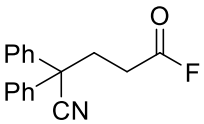
***N*-benzyl-3-ethylheptanamide (5yy).** 73% yield (36.0 mg, 0.14 mmol). Pale yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.30 (m, 2H), 7.30 – 7.26 (m, 3H), 5.74 (s, 1H), 4.50 – 4.39 (m, 2H), 2.20 – 2.06 (m, 2H), 1.91 – 1.79 (m, 1H), 1.41 – 1.21 (m, 8H), 0.93 – 0.82 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.7, 138.5, 128.7, 127.9, 127.5, 43.6, 41.6, 36.8, 33.0, 28.8, 26.2, 23.0, 14.1, 10.8. HRMS: calculated for $C_{16}H_{25}NONa^+$ ($M+Na^+$): 270.1828, found: 270.1821.



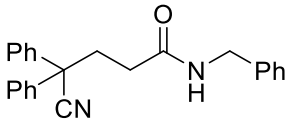
3-Methoxypropanoyl fluoride (1zz). *In situ* NMR data: ^{1}H NMR (500 MHz, CD_3CN) δ 3.62 (td, *J* = 6.0, 1.0 Hz, 2H), 3.31 (s, 3H), 2.80 (td, *J* = 5.9, 1.7 Hz, 2H). ^{13}C NMR (126 MHz, CD_3CN) δ 162.2 (d, *J* = 358.8 Hz), 66.4 (d, *J* = 2.4 Hz), 58.0, 33.0 (d, *J* = 51.7 Hz). ^{19}F NMR (377 MHz, CD_3CN) δ 43.32.



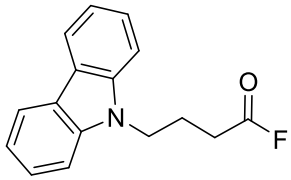
***N*-benzyl-3-methoxypropanamide (5zz).** 68% yield (26.3 mg, 0.14 mmol). Yellow oil. Spectral data correlated with that previously reported in the literature.[53] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 2H), 7.26 (d, *J* = 7.5 Hz, 3H), 6.48 (s, 1H), 4.46 (d, *J* = 5.8 Hz, 2H), 3.66 (t, *J* = 5.9 Hz, 2H), 3.36 (s, 3H), 2.51 (t, *J* = 5.8 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.3, 138.4, 128.7, 127.6, 127.4, 68.7, 58.8, 43.4, 37.1.



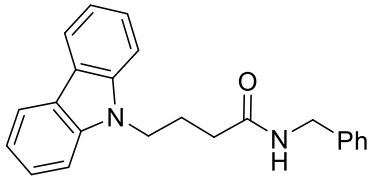
4-Cyano-4,4-diphenylbutanoyl fluoride (1aaa). *In situ* NMR data: ^{1}H NMR (500 MHz, CD_3CN) δ 7.46 – 7.40 (m, 10H), 2.87 – 2.81 (m, 2H), 2.68 – 2.62 (m, 2H). ^{13}C NMR (126 MHz, CD_3CN) δ 162.7 (d, *J* = 357.2 Hz), 139.3, 129.2, 128.4, 126.6, 121.4, 41.5, 32.6 (d, *J* = 3.3 Hz), 28.8 (d, *J* = 54.5 Hz).^{19}F NMR (377 MHz, CD_3CN) δ 42.96.



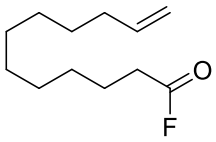
***N*-benzyl-4-cyano-4,4-diphenylbutanamide (5aaa).** 62% yield (44.3 mg, 0.12 mmol). Yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.39 (m, 4H), 7.38 – 7.35 (m, 3H), 7.35 – 7.26 (m, 6H), 7.25 – 7.22 (m, 2H), 5.67 (s, 1H), 4.39 (d, *J* = 5.7 Hz, 2H), 2.86 – 2.80 (m, 2H), 2.37 – 2.31 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.8, 139.5, 137.9, 129.0, 128.8, 128.1, 127.9, 127.7, 126.8, 122.0, 51.1, 43.8, 34.8, 32.7. HRMS: calculated for $C_{24}H_{22}N_2ONa^+$ ($M+Na^+$): 377.1624, found: 377.1621.



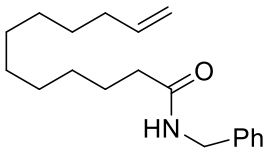
4-(9H-carbazol-9-yl)butanoyl fluoride (1bbb). *In situ* NMR data: ^{1}H NMR (500 MHz, CD_3CN) δ 8.13 (dt, *J* = 7.9, 1.1 Hz, 2H), 7.53 – 7.50 (m, 2H), 7.48 – 7.46 (m, 2H), 7.23 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 2H), 4.42 (t, *J* = 7.2 Hz, 2H), 2.62 (td, *J* = 7.2 Hz, J^{H-F} = 0.9 Hz, 2H), 2.17 (tt, *J* = 7.2, 7.2 Hz, 2H) ppm. ^{13}C NMR (126 MHz, CD_3CN) δ 164.6 (d, *J* = 358.4 Hz), 141.2, 126.8, 123.6, 121.2, 120.0, 109.8, 42.1, 30.7 (*J* = 52.1 Hz), 23.9 (d, *J* = 3.1 Hz) ppm. ^{19}F NMR (377 MHz, CD_3CN) δ 43.0 ppm.



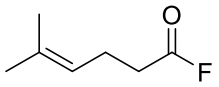
N-benzyl-4-(9H-carbazol-9-yl)butanamide (5bbb) 70% yield (47 mg, 0.14 mmol). Yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.8 Hz, 2H), 7.47 – 7.41 (m, 4H), 7.37 – 7.33 (m, 2H), 7.32 - 7.28 (m, 1H), 7.27 – 7.24 (m, 4H), 5.62 (br t, *J* = 5.8 Hz, 1H), 4.41 (t, *J* = 6.7 Hz, 2H), 4.40 (d, *J* = 5.7 Hz, 2H), 2.28 (tt, *J* = 6.9 Hz, 6.8 Hz, 2H), 2.14 (t, *J* = 7.0 Hz, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.7, 140.5, 138.2, 128.8, 128.0, 127.6, 125.8, 122.9, 120.4, 119.0, 108.8, 43.7, 42.0, 32.8, 24.5. HRMS (ESI^+): calculated for $C_{23}H_{22}N_2ONa^+$: 365.1624, found 365.1620.



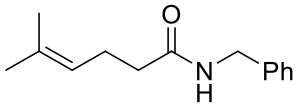
Dodec-11-enoyl fluoride (1ccc). *In situ* NMR data: ^{1}H NMR (500 MHz, CD_3CN) δ 5.83 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.00 (ddt, *J* = 17.2, 3.8, 2.2 Hz, 1H), 4.92 (ddt, *J* = 10.2, 2.4, 1.2 Hz, 1H), 2.55 (t, *J* = 7.4 Hz, 2H), 2.08 – 1.99 (m, 2H), 1.62 (p, *J* = 7.3 Hz, 2H), 1.39 – 1.27 (m, 12H). ^{13}C NMR (126 MHz, CD_3CN) δ 164.1 (d, *J* = 359.0 Hz), 139.3, 113.7, 33.5, 31.6 (d, *J* = 49.9 Hz), 29.1, 29.0, 28.8, 28.8, 28.7, 28.3, 23.6 (d, *J* = 2.3 Hz). ^{19}F NMR (377 MHz, CD_3CN) δ 43.05.



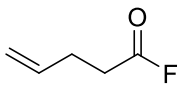
***N*-benzyldodec-11-enamide (5ccc).** 77% yield (44.1 mg, 0.15 mmol). Yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 2H), 7.30 – 7.25 (m, 3H), 5.81 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.74 (s, 1H), 5.01 (ddt, *J* = 17.1, 1.7, 1.7 Hz, 1H), 4.93 (ddt, *J* = 10.2, 2.1, 2.1 Hz, 1H), 4.44 (d, *J* = 5.7 Hz, 2H), 2.26 – 2.18 (m, 2H), 2.09 – 1.98 (m, 2H), 1.65 (tt, *J* = 7.5, 7.3 Hz, 2H), 1.41 – 1.23 (m, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.0, 139.2, 138.5, 128.7, 127.8, 127.5, 114.1, 43.6, 36.8, 33.8, 29.4 (two signals overlapped), 29.3, 29.3, 29.1, 28.9, 25.8. HRMS: calculated for $C_{19}H_{29}NONa^+$ ($M+Na^+$): 310.2141, found: 310.2149.



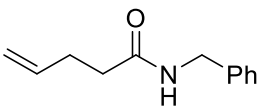
5-Methylhex-4-enoyl fluoride (1ddd). *In situ* NMR data: ^{1}H NMR (500 MHz, CD_3CN) δ 5.14 – 5.09 (m, 1H), 2.58 (t, *J* = 7.1 Hz, 2H), 2.36 – 2.27 (m, 2H), 1.69 (d, *J* = 1.4 Hz, 3H), 1.63 (d, *J* = 1.3 Hz, 3H). ^{13}C NMR (126 MHz, CD_3CN) δ 163.7 (d, *J* = 359.7 Hz), 133.7 (d, *J* = 50.9 Hz), 121.3, 31.9 (d, *J* = 49.5 Hz), 24.8, 22.3 (d, *J* = 2.5 Hz), 16.7. ^{19}F NMR (377 MHz, CD_3CN) δ 43.03.



***N*-benzyl-5-methylhex-4-enamide (5ddd).** 64% yield (27.6 mg, 0.13 mmol). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 2H), 7.30 – 7.25 (m, 3H), 5.74 (s, 1H), 5.10 (th, *J* = 7.1, 1.4, 1H), 4.44 (d, *J* = 5.7 Hz, 2H), 2.34 (t, *J* = 7.4 Hz, 2H), 2.24 (td, *J* = 7.7, 0.9 Hz, 2H), 1.67 (d, *J* = 1.4 Hz, 3H), 1.60 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.5, 138.4, 133.4, 128.7, 127.8, 127.5, 122.7, 43.6, 36.8, 25.7, 24.3, 17.7. HRMS: calculated for $C_{14}H_{19}NONa^+$ ($M+Na^+$): 240.1359, found: 240.1349.

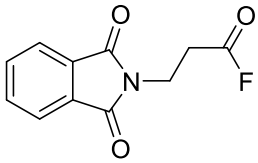


Pent-4-enoyl fluoride (1eee). 4-bromobutene (13.5 mg, 0.10 mmol) was used as the substrate. Spectra data are the same as **1b.** *In situ* NMR data: ^{1}H NMR (500 MHz, CD_3CN) δ 5.86 (ddt, *J* = 17.3, 10.3, 6.5 Hz, 1H), 5.12 (ddt, *J* = 17.2, 1.7, 1.7 Hz, 1H), 5.05 (ddt, *J* = 10.3, 1.4, 1.4 Hz, 1H), 2.67 (t, *J* = 7.3 Hz, 2H), 2.41 – 2.36 (m, 2H). ^{13}C NMR (126 MHz, CD_3CN) δ 163.5 (d, *J* = 359.2 Hz), 135.8, 115.7, 31.0 (d, *J* = 50.8 Hz), 27.4 (d, *J* = 2.8 Hz). ^{19}F NMR (377 MHz, CD_3CN) δ 42.95.

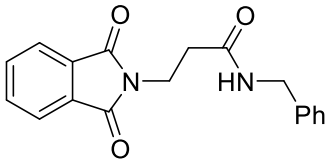


***N*-benzylpent-4-enamide (5eee)**. 48% yield (18.0 mg, 0.10 mmol). 4-bromobutene (27.0 mg, 0.20 mmol) was used as the substrate. Pale yellow liquid. Spectra data are the same as **5b.** Spectral data correlated with that

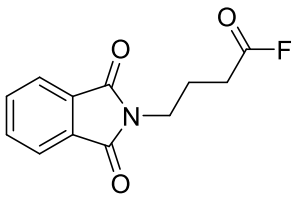
previously reported in the literature.[5] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 2H), 7.30 – 7.26 (m, 3H), 5.83 (ddt, *J* = 16.8, 10.2, 6.5 Hz, 1H), 5.75 (s, 1H), 5.07 (ddt, *J* = 17.1, 1.7, 1.7 Hz, 1H), 5.01 (ddt, *J* = 10.2, 1.7, 1.7 Hz, 1H), 4.44 (d, *J* = 5.7 Hz, 2H), 2.46 – 2.37 (m, 2H), 2.33 – 2.29 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.0, 138.3, 137.0, 128.7, 127.8, 127.5, 115.7, 43.6, 35.9, 29.6.



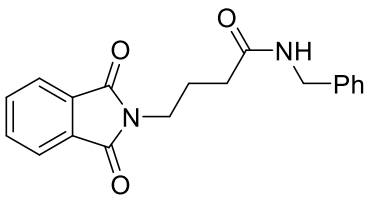
3-(1,3-Dioxoisoindolin-2-yl)propanoyl fluoride (1fff). *In situ* NMR data: ^{1}H NMR (500 MHz, CD_3CN) δ 7.87 – 7.82 (m, 2H), 7.82 – 7.78 (m, 2H), 3.93 (t, *J* = 6.8 Hz, 2H), 2.99 (t, *J* = 6.8 Hz, 2H). ^{13}C NMR (126 MHz, CD_3CN) δ 167.9, 161.8 (d, *J* = 358.0 Hz), 134.3, 132.1, 123.0, 32.5 (d, *J* = 3.9 Hz), 30.7 (d, *J* = 53.1 Hz). ^{19}F NMR (377 MHz, CD_3CN) δ 43.26.



***N*-benzyl-3-(1,3-dioxoisoindolin-2-yl)propanamide (5fff).** 80% yield (49.4 mg, 0.16 mmol). Pale yellow solid. Spectral data correlated with that previously reported in the literature.[54] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.72 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.30 – 7.21 (m, 5H), 5.90 (s, 1H), 4.42 (d, *J* = 5.7 Hz, 2H), 4.04 (t, *J* = 7.2 Hz, 2H), 2.67 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.4, 168.2, 138.0, 134.0, 132.0, 128.7, 127.9, 127.6, 123.4, 43.7, 34.8, 34.4.

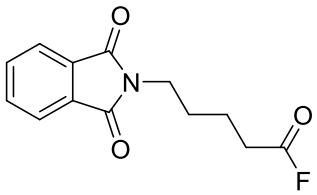


4-(1,3-Dioxoisoindolin-2-yl)butanoyl fluoride (1ggg). *In situ* NMR data: ^{1}H NMR (500 MHz, CD_3CN) δ 7.85 – 7.81 (m, 2H), 7.80 – 7.77 (m, 2H), 3.70 (td, *J* = 6.7, 1.0 Hz, 2H), 2.64 (td, *J* = 7.2, 1.3 Hz, 2H), 1.98 (tt, *J* = 7.0, 6.9 Hz, 2H). ^{13}C NMR (126 MHz, CD_3CN) δ 168.5, 163.6 (d, *J* = 358.3 Hz), 134.2, 132.2, 122.9, 36.2, 29.1 (d, *J* = 52.1 Hz), 22.8 (d, *J* = 3.6 Hz). ^{19}F NMR (377 MHz, CD_3CN) δ 42.71.

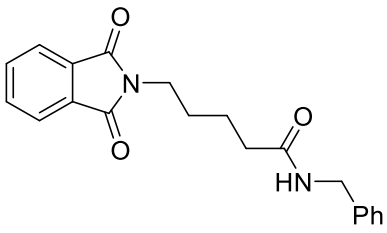


***N*-benzyl-4-(1,3-dioxoisoindolin-2-yl)butanamide (5ggg).** 71% yield (45.6 mg, 0.14 mmol). Pale yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.71 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.35 – 7.24 (m, 5H), 6.23 (s, 1H), 4.42 (d, *J* = 5.7 Hz, 2H), 3.74 (t, *J* = 6.4 Hz, 2H), 2.25 (t, *J* = 7.2 Hz, 2H), 2.02 – 2.09 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$)

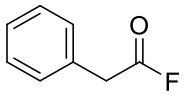
δ 171.7, 168.6, 138.3, 134.1, 132.0, 128.7, 127.8, 127.4, 123.3, 43.7, 37.3, 33.8, 25.1. HRMS: calculated for $C_{19}H_{18}N_2O_3Na^+$ ($M+Na^+$): 345.1210, found: 345.1198.



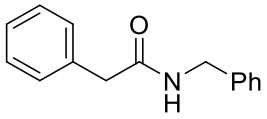
5-(1,3-Dioxoisoindolin-2-yl)pentanoyl fluoride (1hhh). *In situ* NMR data: ^{1}H NMR (500 MHz, CD_3CN) δ 7.83 – 7.80 (m, 2H), 7.79 – 7.76 (m, 2H), 3.64 (td, *J* = 6.8, 2.1 Hz, 2H), 2.61 (t, *J* = 7.2 Hz, 2H), 1.75 – 1.59 (m, 4H). ^{13}C NMR (126 MHz, CD_3CN) δ 168.4, 163.9 (d, *J* = 358.9 Hz), 134.1, 132.2, 122.8, 37.0, 31.0 (d, *J* = 50.5 Hz), 27.1, 21.0 (d, *J* = 2.8 Hz). ^{19}F NMR (377 MHz, CD_3CN) δ 42.99.



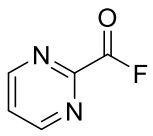
***N*-benzyl-5-(1,3-dioxoisoindolin-2-yl)pentanamide (5hhh).** 74% yield (47.8 mg, 0.15 mmol). Colorless solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.70 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.34 – 7.29 (m, 2H), 7.28 – 7.23 (m, 3H), 5.87 (s, 1H), 4.42 (d, *J* = 5.7 Hz, 2H), 3.70 (t, *J* = 6.7 Hz, 2H), 2.28 (t, *J* = 7.3 Hz, 2H), 1.80 – 1.62 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.3, 168.5, 138.4, 134.0, 132.1, 128.7, 127.8, 127.5, 123.2, 43.6, 37.2, 35.9, 28.0, 22.9. HRMS: calculated for $C_{20}H_{20}N_2O_3Na^+$ ($M+Na^+$): 359.1366, found: 359.1357.



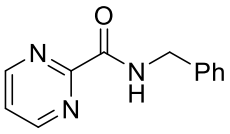
2-Phenylacetyl fluoride (1iii). Benzyl chloride (25.3 mg, 0.20 mmol) was used as the substrate. Spectra data are the same as **1ee**. Spectral data correlated with that previously reported in the literature.[16] *In situ* NMR data: ^{1}H NMR (800 MHz, CD_3CN) δ 7.43 –7.31 (m, 5H, overlapped with BnCl), 3.92 (s, 2H). ^{13}C NMR (201 MHz, CD_3CN) δ 163.4 (d, *J* = 359.6 Hz), 130.5, 129.7, 129.7, 128.7, 39.0 (d, *J* = 55.0 Hz). ^{19}F NMR (377 MHz, CD_3CN) δ 41.89.



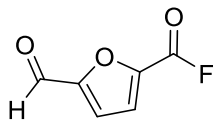
***N*-benzyl-2-phenylacetamide (5iii).** 54% yield (24.3 mg, 0.11 mmol). Benzyl chloride (25.3 mg, 0.20 mmol) was used as the substrate. Yellow solid. Spectral data are the same as **5ee.** Spectral data correlated with that previously reported in the literature.[39] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.32 (m, 2H), 7.32 – 7.22 (m, 6H), 7.20 – 7.15 (m, 2H), 5.76 (s, 1H), 4.41 (d, *J* = 5.8 Hz, 2H), 3.62 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.9, 138.2, 134.8, 129.5, 129.1, 128.7, 127.5, 127.4, 127.4, 43.9, 43.6.



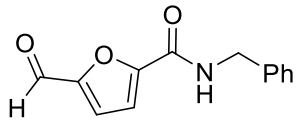
Pyrimidine-2-carbonyl fluoride (4a). *In situ* NMR data: ^{1}H NMR (800 MHz, CH_3CN) δ 8.95 (d, *J* = 5.0 Hz, 2H), 7.64 (t, *J* = 4.9 Hz, 1H) ppm. ^{13}C NMR (201 MHz, CD_3CN) δ 160.7, 159.2, 154.4 (d, *J* = 307.1 Hz), 153.4 (d, *J* = 77.8 Hz). ^{19}F NMR (201 MHz, CD_3CN) δ 17.1 ppm.



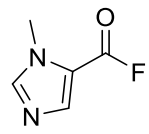
***N*–Benzylpyrmidine-2-carboxamide (7a).** 62% yield (26 mg, 0.12 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.85 (d, *J* = 4.9 Hz, 2H), 8.30 (brs, 1H), 7.42 (t, *J* = 4.9 Hz, 1H), 7.37 – 7.32 (m, 4H), 7.30 – 7.25 (m, 1H), 4.71(d, *J* = 6.0 Hz, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.2, 157.7, 157.5, 137.8, 128.8, 128.0, 127.7, 122.6, 44.0 ppm. HRMS (ESI^+): calculated for $C_{12}H_{12}N_3O^+$: 214.0975, found 214.09711.



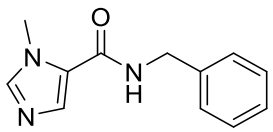
5-formylfuran-2-carbonyl fluoride (4b). *In situ* NMR data: ^{1}H NMR (500 MHz, CD_3CN) δ 9.79 (s, 1H), 7.62 (d, *J* = 3.8 Hz, 1H), 7.47 (dd, *J* = 3.8 Hz, $J_{H\text{-}F}$ = 0.7 Hz, 1H) ppm. ^{13}C NMR (126 MHz, CD_3CN) δ 180.4, 156.4 (d, *J* = 2.5 Hz), 149.0 (d, *J* = 330.0 Hz), 142.4 (d, *J* = 91.0 Hz), 124.9, 121.9 ppm. ^{19}F NMR (377 MHz, CD_3CN) δ 17.2 ppm.



N-benzyl-5-formylfuran-2-carboxamide (7b). 84 % yield (38 mg, 0.168 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.67 (s, 1H), 7.36 – 7.34 (m, 4H), 7.32 -7.30 (m, 1H), 7.28 (d, *J* = 3.7 Hz, 1H), 7.27 (d, *J* = 3.7 Hz, 1H), 7.00 (brs, 1H), 4.62 (d, *J* = 6.0 Hz, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.0, 157.3, 152.3, 151.3, 137.3, 128.9, 128.2, 128.0, 122.4, 115.8, 43.6 ppm. HRMS (ESI^+): calculated for $C_{13}H_{11}NO_3Na^+$: 252.0631, found 252.0626.

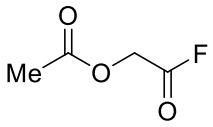


1-Methyl-1H-imidazole-5-carbonyl fluoride (4c). *In situ* NMR data: ^{1}H NMR (500 MHz, CD_3CN) δ 7.36 (s, 1H), 6.91 (s, 1H), 3.85 (s, 3H). ^{13}C NMR (126 MHz, CD_3CN) δ 150.0 (d, *J* = 323.1 Hz), 141.6 (s), 127.9 (d, *J* = 6.6 Hz), 33.4 (s). ^{19}F NMR (471 MHz, CD_3CN) δ 20.1.

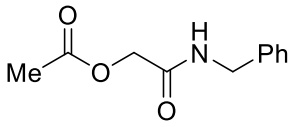


***N*-benzyl-1-methyl-1H-imidazole-5-carboxamide (7c).** 63% NMR yield, 30% isolated yield (13.0 mg, 0.06 mmol). White solid. ^{1}H NMR (800 MHz, $CDCl_3$) δ 7.48 (s, 1H), 7.41 (s, 1H), 7.36 – 7.32 (m, 4H), 7.30 (t, *J* = 7.1 Hz, 1H), 6.29 (brs, 1H), 4.58 (d, *J* = 5.8 Hz), 3.95 (s, 3H). ^{13}C NMR (201 MHz, $CDCl_3$) δ 160.3,

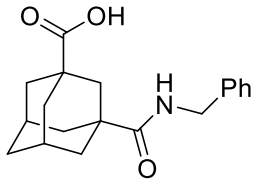
141.8, 138.0, 131.5, 128.9, 127.8, 127.7, 126.1, 43.3, 34.1. HRMS: calculated for $C_{12}H_{13}N_3ONa^+$ ($M+Na^+$): 238.0956, found: 238.0954.



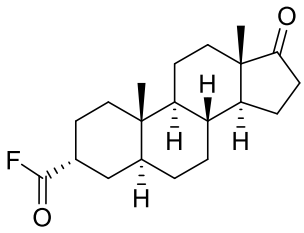
2-Fluoro-2-oxoethyl acetate (4d). *In situ* NMR data: ^{1}H NMR (500 MHz, CD_3CN) δ 4.81 (d, *J* = 3.4 Hz, 2H), 2.13 (s, 3H). ^{13}C NMR (126 MHz, CD_3CN) δ 170.1, 159.1 (d, *J* = 359.4 Hz), 58.5 (d, *J* = 75.8 Hz), 19.4. ^{19}F NMR (377 MHz, CD_3CN) δ 27.16.



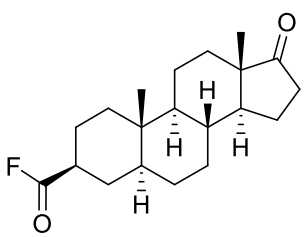
2-(Benzylamino)-2-oxoethyl acetate (7d). 47% yield (19.4 mg, 0.09 mmol). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 2H), 7.34 – 7.28 (m, 3H), 6.40 (s, 1H), 4.62 (s, 2H), 4.51 (d, *J* = 5.8 Hz, 2H), 2.14 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.3, 166.85, 137.6, 128.8, 127.9, 127.8, 63.1, 43.2, 20.8. HRMS: calculated for $C_{11}H_{13}NO_3Na^+$ ($M+Na^+$): 230.0788, found: 230.0787.



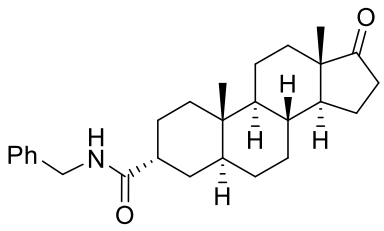
3-(benzylcarbamoyl)adamantane-1-carboxylic acid (4e). 56% yield (35 mg, 0.112 mmol). White solid. ^{1}H NMR (500 MHz, MeOD) δ 7.33 – 7.18 (m, 5H), 4.37 (s, 2H), 2.12 (brtt, *J* = 3.1, 3.1 Hz, 2H), 1.98 (s, 2H), 1.92 – 1.81 (m, 8H), 1.75 – 1.66 (m, 2H). ^{13}C NMR (126 MHz, MeOD) δ 185.1, 180.5, 140.6, 129.3, 128.1, 127.9, 43.7, 43.4, 42.6, 42.6, 40.1, 39.6, 36.9, 30.0. HRMS (ESI^+): calculated for $C_{19}H_{23}NO_3Na^+$: 336.1570, found 336.1576.



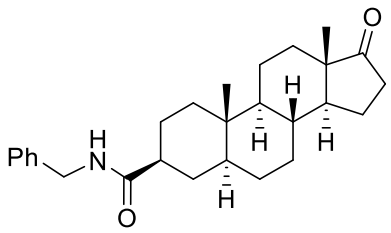
(3R,5S,8R,9S,10S,13S,14S)-10,13-Dimethyl-17-oxohexadecahydro-1H-cyclopenta[a]phenanthrene-3-carbonyl fluoride (4f-1). *In situ* NMR data: ^{1}H NMR (500 MHz, CD_3CN) δ 3.00 (dq, *J* = 5.4, 2.7 Hz, 1H). ^{13}C NMR (126 MHz, CD_3CN) δ 165.7 (d, *J* = 365.4 Hz). ^{19}F NMR (377 MHz, CD_3CN) δ 35.2.



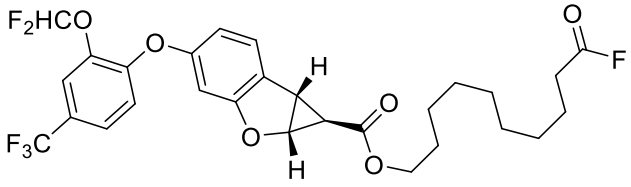
(3S,5S,8R,9S,10S,13S,14S)-10,13-Dimethyl-17-oxohexadecahydro-1H-cyclopenta[a]phenanthrene-3-carbonyl fluoride (4f-2). *In situ* NMR data: ^{1}H NMR (500 MHz, CD_3CN) 2.60 (tt, *J* = 12.5, 4.1 Hz, 1H). ^{13}C NMR (126 MHz, CD_3CN) δ 165.7(d, *J* = 365.4 Hz). ^{19}F NMR (377 MHz, CD_3CN) δ 34.6.



(3R,5S,8R,9S,10S,13S,14S)-*N*-benzyl-10,13-dimethyl-17-oxohexadecahydro-1H-cyclopenta[a]phenanthrene-3-carboxamide (7f-1). 48% isolated (19.5 mg, 0.048 mmol), colorless oil and slowly solidified. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 2H), 7.28 (m, 3H), 5.84 (t, *J* = 5.9 Hz, 1H), 4.46 (d, *J* = 5.7 Hz, 2H), 2.53 (tt, *J* = 5.0, 2.0 Hz, 1H), 2.42 (ddd, *J* = 19.2, 8.9, 1.1 Hz, 1H), 2.06 (dt, *J* = 19.3, 9.1 Hz, 1H), 1.97 – 1.84 (m, 2H), 1.81 – 1.70 (m, 3H), 1.70 – 1.60 (m, 2H), 1.60 – 1.41 (m, 5H), 1.37 – 1.15 (m, 6H), 1.01 (qd, *J* = 12.8, 4.4 Hz, 1H), 0.84 (d, *J* = 10.0 Hz, 6H), 0.78 (td, *J* = 11.7, 4.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.0, 138.7, 128.7, 127.7, 127.5, 54.4, 51.5, 47.8, 43.6, 42.1, 39.7, 36.1, 35.9, 35.0, 34.9, 31.6, 30.7, 30.5, 28.4, 23.5, 21.7, 20.0, 13.8, 11.7. HRMS: calculated for $C_{27}H_{37}NO_2Na^+$ ($M+Na^+$): 430.2717, found: 430.2705.

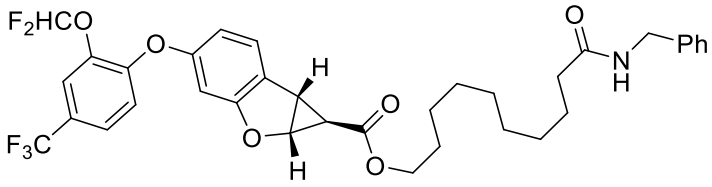


(3S,5S,8R,9S,10S,13S,14S)-*N*-benzyl-10,13-dimethyl-17-oxohexadecahydro-1H-cyclopenta[a]phenanthrene-3-carboxamide (7f-2). 16% isolated (6.5 mg, 0.016 mmol), colorless oil and slowly solidified. ^{1}H NMR (500 MHz, $CDCl_3$) δ ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.33 (m, 2H), 7.31 – 7.23 (m, 3H), 5.70 (t, *J* = 5.5 Hz, 1H), 4.44 (d, *J* = 5.6 Hz, 2H), 2.43 (ddd, *J* = 19.2, 9.0, 1.1 Hz, 1H), δ 2.14 (tt, J = 12.0, 4.4 Hz, 1H), 2.10 – 2.00 (m, 1H), 1.98 – 1.88 (m, 1H), 1.84 – 1.74 (m, 3H), 1.75 – 1.71 (m, 1H), 1.72 – 1.61 (m, 2H), 1.61 – 1.46 (m, 4H), 1.38 – 1.17 (m, 5H), 1.13 (tt, *J* = 11.8, 3.8 Hz, 1H), 1.06 – 0.90 (m, 2H), 0.85 (d, *J* = 2.3 Hz, 6H), 0.72 (ddd, *J* = 12.2, 10.4, 4.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.6, 127.8, 127.5, 54.5, 51.5, 47.8, 46.2, 45.9, 43.5, 37.9, 36.0, 35.8, 35.0, 31.8, 31.6, 30.9, 28.4, 25.3, 21.8, 20.2, 13.8, 12.3. HRMS: calculated for $C_{27}H_{37}NO_2Na^+$ ($M+Na^+$): 430.2717, found: 430.2705.

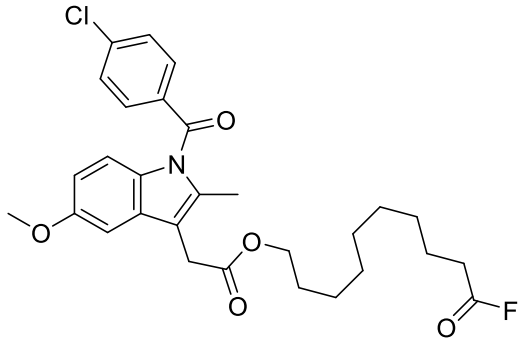


10-Fluoro-10-oxodecyl (1*R*,1a*R*,6b*S*)-4-(2-(difluoromethoxy)-4-(trifluoromethyl)phenoxy)-1a,6b-dihydro-1*H*-cyclopropa[*b*]benzofuran-1-carboxylate (4g). *In situ* NMR data: ^{1}H NMR

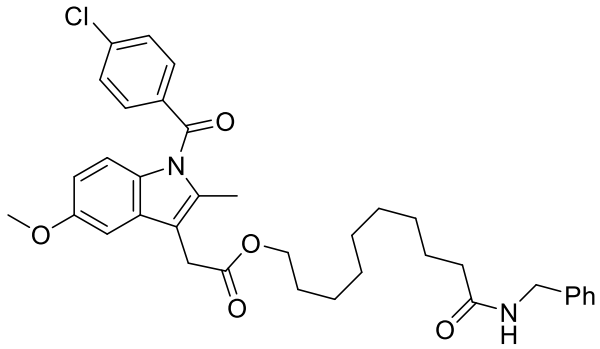
(500 MHz, CH_3CN) δ 7.59 (d, *J* = 2.2 Hz, 1H), 7.49 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.42 (d, *J* = 8.9 Hz, 1H), 7.04 (d, *J* = 8.6 Hz, 1H), 6.86 (t, $J^{H\text{-}F}$= 73.8 Hz, 1H), 6.63 (d, *J* = 6.9 Hz, 2H), 5.12 (dd, *J* = 5.5, 1.1 Hz, 1H), 4.06 (t, *J* = 6.6 Hz, 2H), 3.55 (td, *J* = 6.7, 2.0 Hz, 1H), 3.27 (dd, *J* = 5.5, 3.1 Hz, 1H), 2.52 (t, *J* = 7.4 Hz, 2H), 1.75 – 1.57 (6H, overlapped by solvent and TBDS peak), 1.35 – 1.24 (8H, overlapped by TBDS peak). ^{13}C NMR (126 MHz, CH_3CN) δ 171.6, 164.6 (d, *J* = 359.3 Hz), 161.2, 156.1, 152.4, 141.9 (t, *J* = 3.4 Hz), 125.9, 125.8 (q, *J* = 32.9 Hz), 125.7, 124.6 (t, *J* = 4.0 Hz), 124.3 (q, *J* = 270.3 Hz), 120.3, 120.0 (q, *J* = 3.8 Hz), 117.0 (t, *J* = 258.6 Hz), 112.7, 102.8, 68.5, 65.4, 32.9 (d, *J* = 1.4 Hz), 32.13 (d, *J* = 49.9 Hz), 29.7, 29.6, 29.5, 29.0 (d, *J* = 56.8 Hz), 28.9, 27.0 (d, *J* = 1.6 Hz), 24.9 (d, *J* = 270.4 Hz), 24.1 (d, *J* = 2.3 Hz). ^{19}F NMR (471 MHz, CH_3CN) δ 44.0, -61.6, -82.4.



10-(Benzylamino)-10-oxodecyl (1*R*,1a*R*,6b*S*)-4-(2-(difluoromethoxy)-4-(trifluoromethyl)phenoxy)-1a,6b-dihydro-1*H*-cyclopropa[*b*]benzofuran-1-carboxylate (7g). 69 % isolated yield (92 mg, 0.139 mmol). Brown solid. ^{1}H NMR (800 MHz, $CDCl_3$) δ 7.45 (d, *J* = 2.2 Hz, 1H), 7.34 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.29 (d, *J* = 8.2 Hz, 1H), 7.27 – 7.24 (m, 2H), 7.21 – 7.19 (m, 3H), 6.92 (d, *J* = 8.6 Hz, 1H), 6.52 (dd, *J* = 8.6, 2.3 Hz, 1H), 6.52 (t, $J^{H\text{-}F}$ = 73.6 Hz, 1H), 6.50 (d, *J* = 2.2 Hz, 1H), 5.65 (brt, *J* = 5.9 Hz, 1H), 5.04 (dd, *J* = 5.5, 1.2 Hz, 1H), 4.37 (d, *J* = 5.7 Hz, 2H), 4.03 (td, *J* = 6.8, 2.2 Hz, 2H), 3.18 (dd, *J* = 5.5, 3.2 Hz, 1H), 2.13 (t, *z* = 7.6 Hz, 2H), 1.61 – 1.53 (m, 4H), 1.25 (dd, *J* = 3.2, 1.2 Hz, 1H) 1.30 – 1.18 (m, 10H). ^{13}C NMR (201 MHz, $CDCl_3$) δ 173.0, 171.7, 160.9, 155.9, 151.8, 141.1 (t, *J* = 3.1 Hz), 138.5, 128.8, 127.9, 127.6, 126.2 (q, *J* = 33.6 Hz), 125.2, 124.9, 124.0 (q, *J* = 3.8 Hz), 123.46 (q, *J* = 273.1 Hz), 120.6 (q, *J* = 3.7 Hz), 119.7, 115.6 (t, *J* = 262.7 Hz), 112.1, 102.5, 68.3, 65.4, 43.7, 36.9, 29.7, 29.4, 29.3, 29.3, 29.2, 28.7, 25.9, 25.8, 23.8. ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.0, -81.8. HRMS (ESI^+): calculated for $C_{35}H_{36}F_5NO_6Na^+$: 684.2355, found 684.2368.

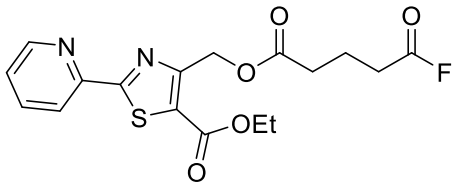


10-fluoro-10-oxodecyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetate (4h). *In situ* NMR data: ^{1}H NMR (500 MHz, CH_3CN) δ 7.59 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 6.98 (d, *J* = 2.6 Hz, 1H), 6.95 (d, *J* = 9.0 Hz, 1H), 6.65 (dd, *J* = 9.1, 2.5 Hz, 1H), 4.03 (t, *J* = 6.5 Hz, 2H), 3.76 (s, 3H), 3.66 (s, 2H), 2.51 (t, *J* = 7.3 Hz, 2H), 2.23 (s, 3H), 1.97-1.89 (2H overlapped by solvent peak), 1.58 – 1.51 (4H overlapped by TBDS peak), 1.25 – 1.13 (m, 8H). ^{13}C NMR (126 MHz, CH_3CN) δ 171.3, 168.8, 164.6 (d, *J* = 359.5 Hz, C=O), 156.6, 139.0, 136.3, 135.0, 134.2, 134.0, 131.4, 131.3, 129.0, 128.9, 115.5, 113.6, 112.0, 101.9, 65.1, 55.8, 34.0 (d, *J* = 234.8 Hz), 32.0 (d, *J* = 49.8 Hz), 30.2, 29.4 (d, *J* = 20.5 Hz), 29.2, 28.9, 28.7, 26.0, 24.0 (d, *J* = 2.2 Hz), 13.3. ^{19}F NMR (471 MHz, CH_3CN) δ 44.0.

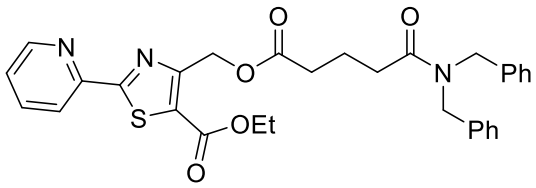


10-(Benzylamino)-10-oxodecyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetate (7h). 67% isolated yield (82 mg, 0.13 mmol). Yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.5 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.35 – 7.30 (m, 2H), 7.29 – 7.25 (m, 3H), 6.97 (d, *J* = 2.6 Hz, 1H), 6.86 (d, *J* = 9.0 Hz, 1H), 6.66 (dd, *J* = 9.0, 2.5 Hz, 1H), 5.76 (brs, 1H), 4.44 (d, *J* = 5.7 Hz, 2H), 4.08 (t, *J* = 6.7 Hz, 2H), 3.83 (s, 3H), 3.65 (s, 2H), 2.38 (s, 3H), 2.19 (t, *J* = 7.7 Hz, 2H), 1.72 – 1.54 (m, 4H), 1.30 – 1.21 (m, 10H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.0, 171.0, 168.4, 156.1, 139.3, 138.5, 135.9, 135.1, 134.0, 131.3, 130.9, 130.8, 129.2, 128.8, 128.0, 127.9, 127.6, 115.0, 112.9, 111.8, 101.4, 65.2, 55.8, 43.7, 36.9, 30.5, 29.4, 29.3, 29.3, 29.2, 28.7, 25.9, 25.8. HRMS (ESI^+): calculated for $C_{36}H_{41}N_2O_5ClNa^+$: 639.2596, found 639.2595.

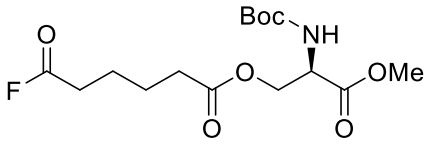
For substrate 4i: 0.4 mmol dibenzylamine was added to trap acyl flouride, and brought to 50 degree for 2 hour before isolation.



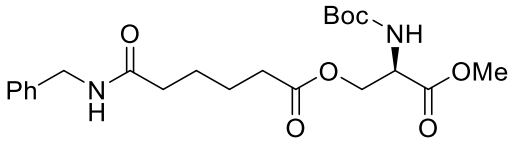
Ethyl 4-(((5-fluoro-5-oxopentanoyl)oxy)methyl)-2-(pyridin-2-yl)thiazole-5-carboxylate (4i). *In situ* NMR data: ^{1}H NMR (500 MHz, CD_3CN) δ 8.59 (ddd, *J* = 4.7, 1.8, 1.0 Hz, 1H), 8.13 (ddd, *J* = 7.9, 4.3, 1.1 Hz, 1H), 7.89 (ddd, *J* = 7.7, 7.7, 1.7 Hz, 1H), 7.46 (ddd, *J* = 7.5, 4.8, 1.2 Hz, 1H), 5.51 (s, 2H), 4.33 (q, *J* = 7.1 Hz, 2H), 3.55 (t, *J* = 6.6 Hz, 2H), 2.56 (t, *J* = 7.1 Hz, 2H), 2.17 (tt, *J* = 6.8, 6.8 Hz, 2H), 0.96 (t, 3H under the big TBDS salt peak) ppm. ^{13}C NMR (126 MHz, CD_3CN) δ 178.9, 173.1, 164.6 (d, *J* = 358.8 Hz, 1C), 162.2, 158.5, 151.0, 150.8, 138.6, 127.4, 127.0, 120.7, 69.5, 61.3, 33.1, 31.6 (d, *J* = 51.3 Hz, 1C), 20.1 (d, *J* = 3.3 Hz), 14.5 ppm. ^{19}F NMR (377 MHz, CD_3CN) δ 43.1 ppm.



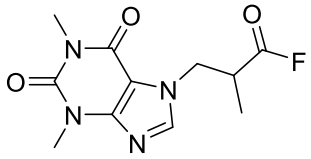
Ethyl 4-(((5-(dibenzylamino)-5-oxopentanoyl)oxy)methyl)-2-(pyridin-2-yl)thiazole-5-carboxylate (7i) 51% yield (57 mg, 0.10 mmol). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.61 (ddd, *J* = 4.8, 1.8, 1.0 Hz, 1H), 8.18 (ddd, *J* = 8.0, 1.0, 1.0 Hz, 1H), 7.76 (ddd, *J* = 7.7, 1.7, 1.7 Hz, 1H), 7.36 (ddd, *J* = 7.7, 4.8, 1.2 Hz, 1H), 7.35 – 7.25 (m, 6H), 7.19 (brd, *J* = 7.1 Hz, 2H), 7.10 (brd, *J* = 6.8 Hz, 2H), 5.56 (s, 2H), 4.58 (s, 2H), 4.42 (s, 2H), 4.34 (q, *J* = 7.1 Hz, 2H), 2.55 (t, *J* = 7.2 Hz, 2H), 2.54(t, *J* = 7.2 Hz, 2H), 2.13 (tt, *J* = 7.2, 7.2 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.0, 172.8, 171.7, 161.5, 157.6, 150.6, 149.7, 137.5, 137.2, 136.6, 129.0, 128.7, 128.3, 127.7, 127.4, 126.8, 126.5, 125.6, 120.3, 61.8, 60.6, 49.9, 48.2, 33.5, 32.3, 20.8, 14.3 ppm. HRMS (ESI^+): calculated for $C_{31}H_{31}N_3O_5SH^+$: 558.2057, found 558.2051.



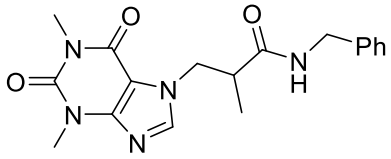
(*R*)-2-((*tert*-butoxycarbonyl)amino)-3-methoxy-3-oxopropyl 6-fluoro-6-oxohexanoate(4j). *In situ* NMR data: ^{1}H NMR (800 MHz, CH_3CN) δ 5.82 (brd, *J* = 8.6 Hz, 1H), 4.40 (brq, *J* = 5.9, 5.4 Hz, 1H), 4.30 – 4.24 (m, 2H), 3.65 (s, 3H), 2.53 (t, *J* = 6.7 Hz, 2H), 2.28 (brt, *J* = 6.8 Hz, 2H), 1.59 – 1.57 (m, 4H), 1.37 (s, 9H). ^{13}C NMR (201 MHz, CH_3CN) δ 173.1, 170.7, 164.3 (d, *J* = 359.2 Hz), 155.8, 79.7, 69.6, 63.8, 53.3, 52.5, 33.4, 31.72 (d, *J* = 50.5 Hz), 28.0, 23.44 (d, *J* = 2.7 Hz). ^{19}F NMR (377 MHz, CH_3CN) δ 43.9.



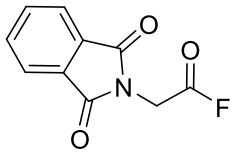
(*R*)-2-((*tert*-butoxycarbonyl)amino)-3-methoxy-3-oxopropyl 6-(benzylamino)-6-oxohexanoate(7j). 58% yield (51mg, 0.116 mmol). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.20 (m, 5H), 6.04 (brs, 1H), 5.40 (d, *J* = 8.6 Hz, 1H), 4.56 (dt, *J* = 8.3, 3.8 Hz, 1H), 4.44 (d, *J* = 5.9 Hz, 2H), 4.42-4.37 (m, 1H), 4.33 (dd, *J* = 11.2, 3.6 Hz, 1H), 3.75 (s, 3H), 2.34 (t, *J* = 6.7 Hz, 2H), 2.23 (t, *J* = 7.0 Hz, 2H), 1.75 – 1.59 (m, 4H), 1.46 (s, 9H). ^{13}C NMR (201 MHz, $CDCl_3$) δ 173.0, 172.4, 170.4, 155.2, 138.4, 135.1, 128.7, 127.9, 127.9, 127.5, 80.4, 64.2, 53.0, 52.8, 43.6, 36.1, 33.6, 28.3, 25.0, 24.3. HRMS (ESI^+): calculated for $C_{22}H_{32}N_2O_7Na^+$: 459.2102, found 459.2112.



3-(1,3-Dimethyl-2,6-dioxo-1,2,3,6-tetrahydro-7H-purin-7-yl)-2-methylpropanoyl fluoride (4k). *In situ* NMR data: ^{1}H NMR (800 MHz, CD_3CN) δ 7.73 (s, 1H), 4.57 (dd, *J* = 14.1, 7.9 Hz, 1H), 4.36 (ddd, *J* = 14.1, 6.4, 2.1 Hz, 1H), 3.47 (s, 3H), 3.28 (s, 3H), 3.27 – 3.23 (m, 1H), 1.26 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (201 MHz, CD_3CN) δ 165.10 (d, *J* = 365.3 Hz), 156.25, 152.55, 150.15, 143.40, 107.71, 48.48, 40.23 (d, *J* = 48.0 Hz), 30.08, 28.16, 13.70. ^{19}F NMR (377 MHz, CD_3CN) δ 37.69.

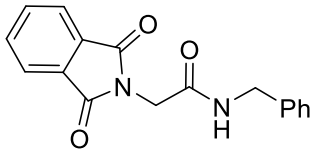


***N*-benzyl-3-(1,3-dimethyl-2,6-dioxo-1,2,3,6-tetrahydro-7H-purin-7-yl)-2-methylpropanamide (7k).** The product was isolated by column chromatography: Silica gel, gradient hexane (with 2% NEt_3)/ethyl acetate 60% to 100%, yield: 72% (25.7 mg, 0.072 mmol), colorless oil and slowly solidified. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.34 – 7.27 (m, 3H), 7.10 (dd, *J* = 7.9, 1.7 Hz, 2H), 6.14 (t, *J* = 5.9 Hz, 1H), 4.47 (dd, *J* = 13.4, 8.5 Hz, 1H), 4.43 – 4.31 (m, 2H), 4.25 (dd, *J* = 13.4, 5.7 Hz, 1H), 3.58 (s, 3H), 3.34 (s, 3H), 2.99 (m, 1H), 1.25 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.9, 155.3, 151.5, 149.2, 142.4, 137.9, 128.7, 127.6, 127.6, 106.6, 50.2, 43.5, 42.4, 29.8, 28.0, 15.4. HRMS: calculated for $C_{18}H_{21}N_5O_3Na^+$ ($M+Na^+$): 378.1537, found: 378.1520.



2-(1,3-Dioxoisoindolin-2-yl)acetyl fluoride (4l). Spectral data correlated with that previously reported in the literature.[55] *In situ* NMR data: ^{1}H NMR (500 MHz, CD_3CN) δ 7.93 – 7.88 (m, 2H), 7.88 – 7.84 (m, 2H), 4.68 (d, *J* =

3.6 Hz, 2H). ^{13}C NMR (126 MHz, CD_3CN) δ 166.9, 159.0 (d, *J* = 361.5 Hz), 134.9, 131.7, 123.6, 37.2 (d, *J* = 74.2 Hz). ^{19}F NMR (471 MHz, CD_3CN) δ 31.69.



***N*-benzyl-2-(1,3-dioxoisoindolin-2-yl)acetamide (7l).** 61% yield (44.9 mg, 0.15 mmol/0.25 mmol), pale yellow solid. Spectral data correlated with that previously reported in the literature.[55] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.75 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.37 – 7.31 (m, 2H), 7.28 (dd, *J* = 7.1, 2.8 Hz, 3H), 5.99 (s, 1H), 4.48 (d, *J* = 5.7 Hz, 2H), 4.38 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.8, 165.9, 137.5, 134.3, 132.0, 128.8, 127.9, 127.7, 123.7, 43.9, 40.9.

8. References

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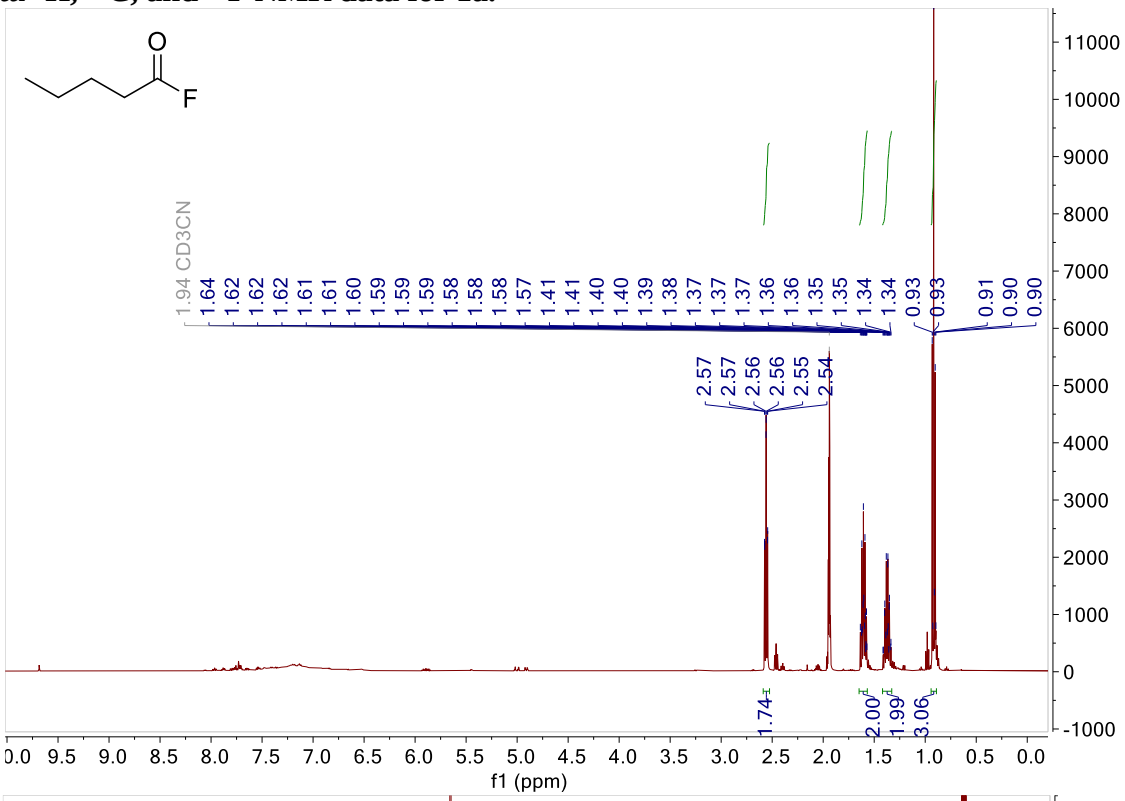
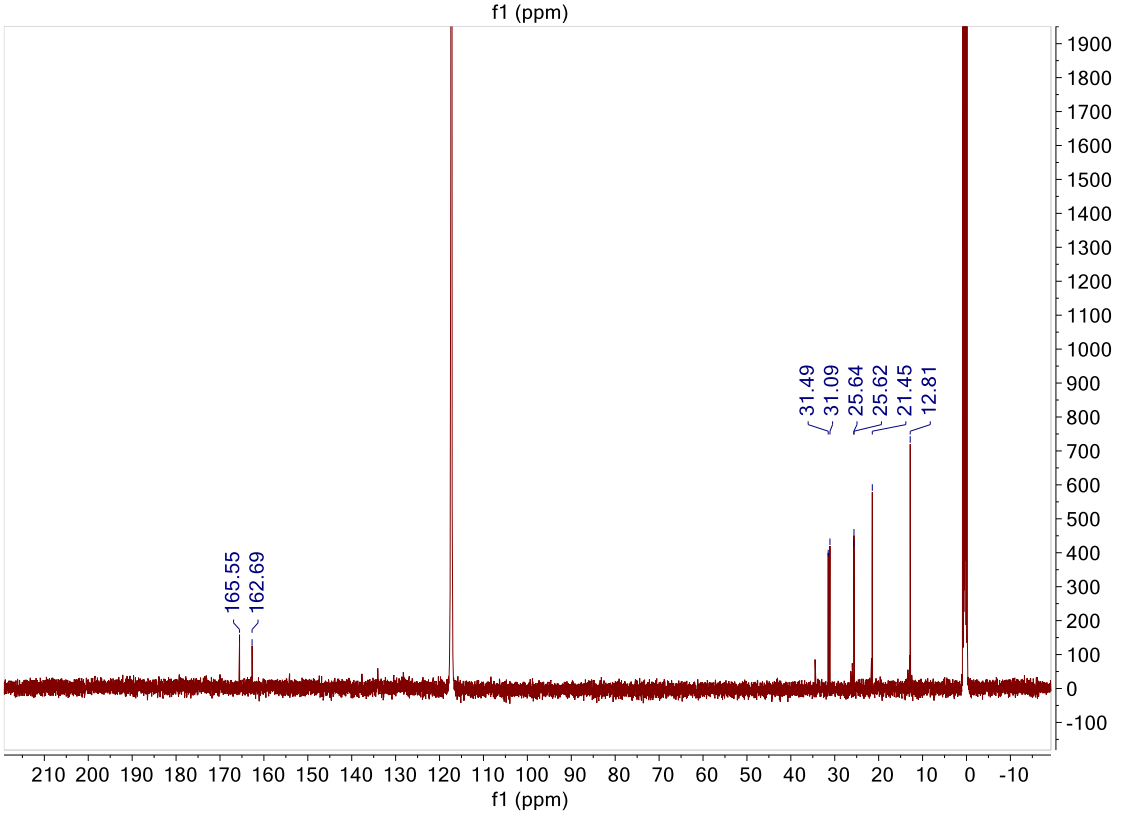
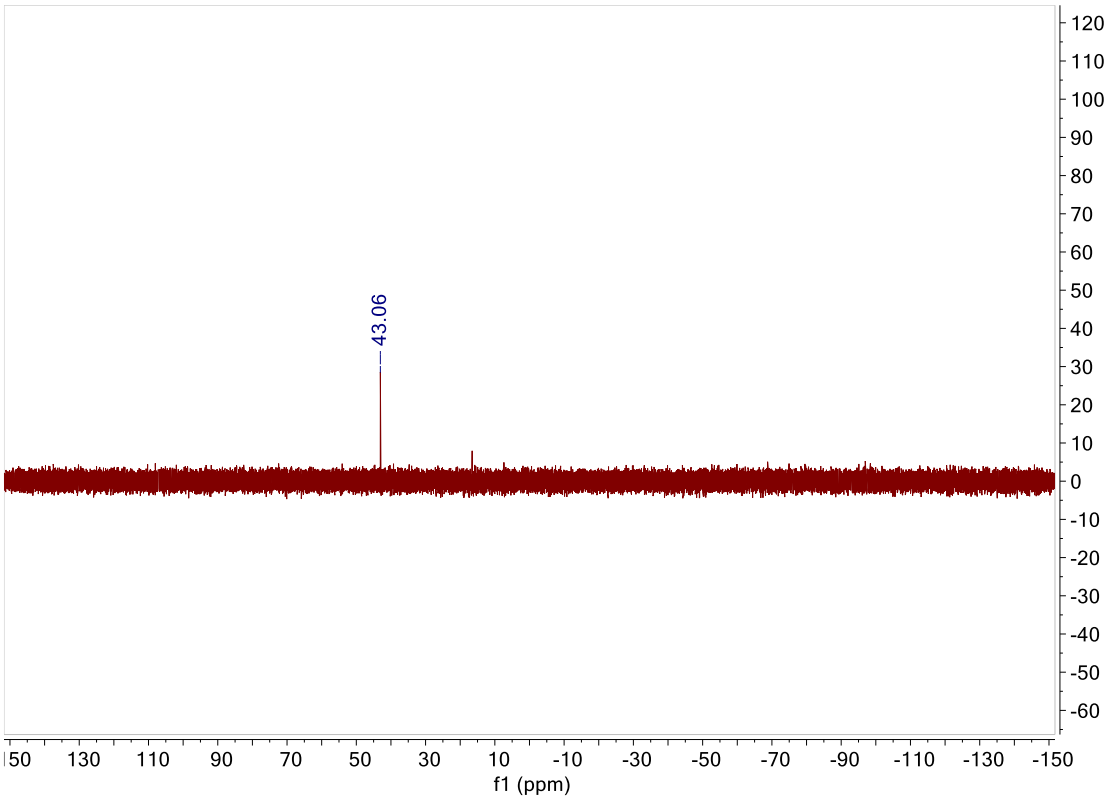
9. NMR Spectra

***In situ* ^{1}H, ^{13}C, and ^{19}F NMR data for 1a.**



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20
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-20
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-60
50
130
110
90
70
50
30
10
-10
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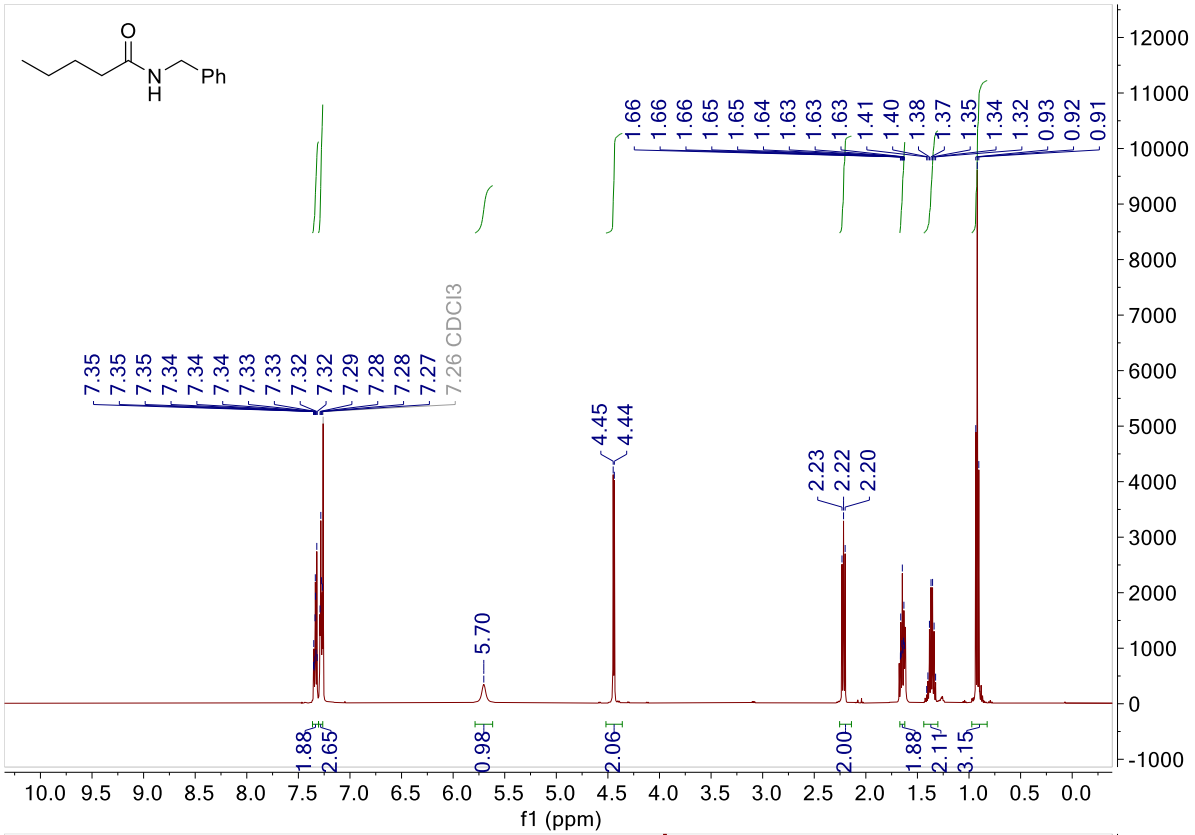
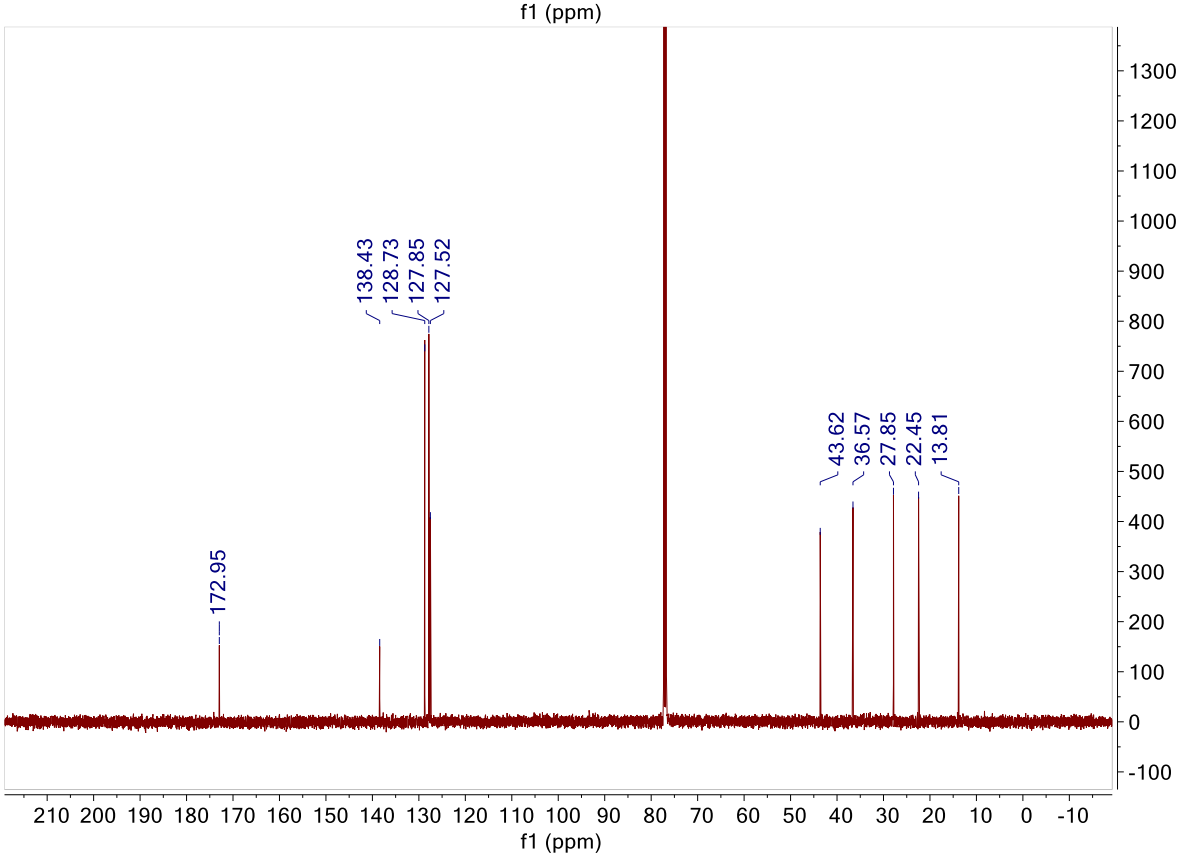
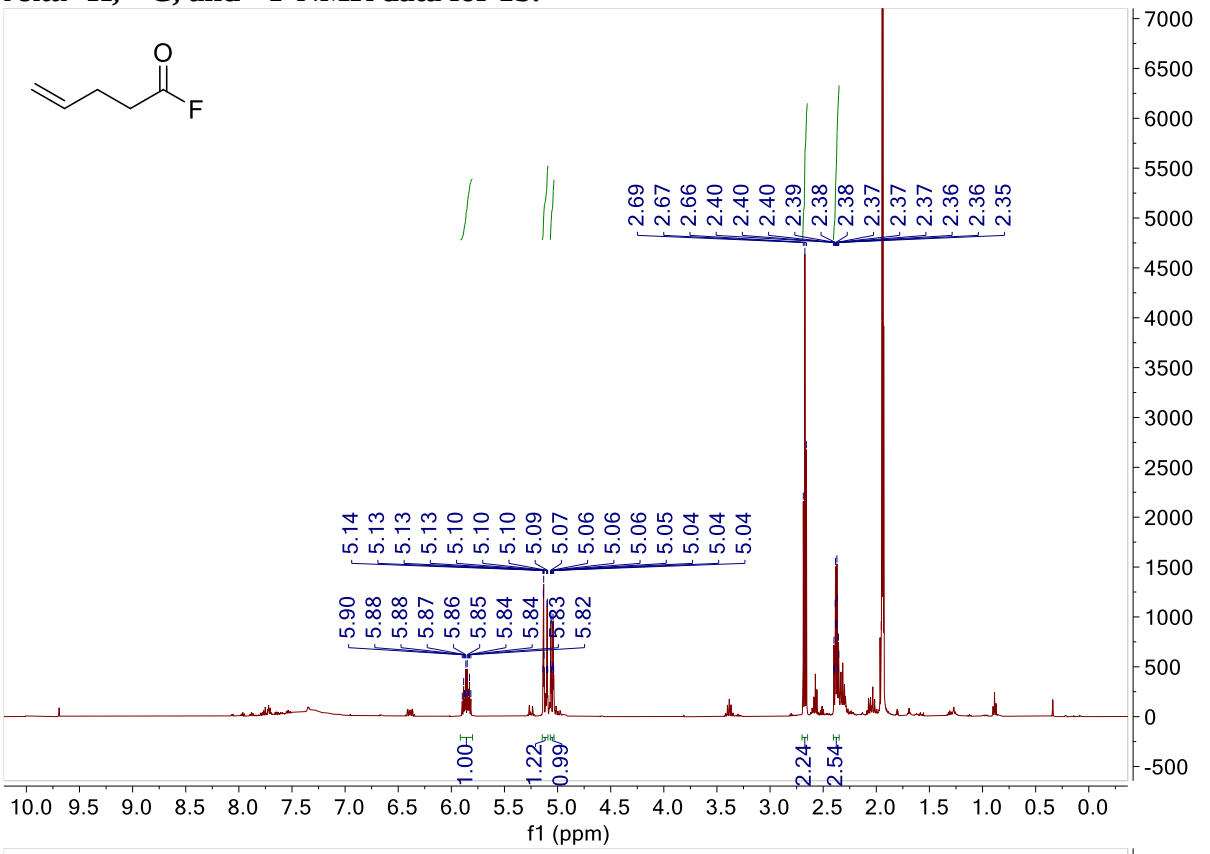
-50
-70
-90
-110
-130
-150
f1 (ppm)

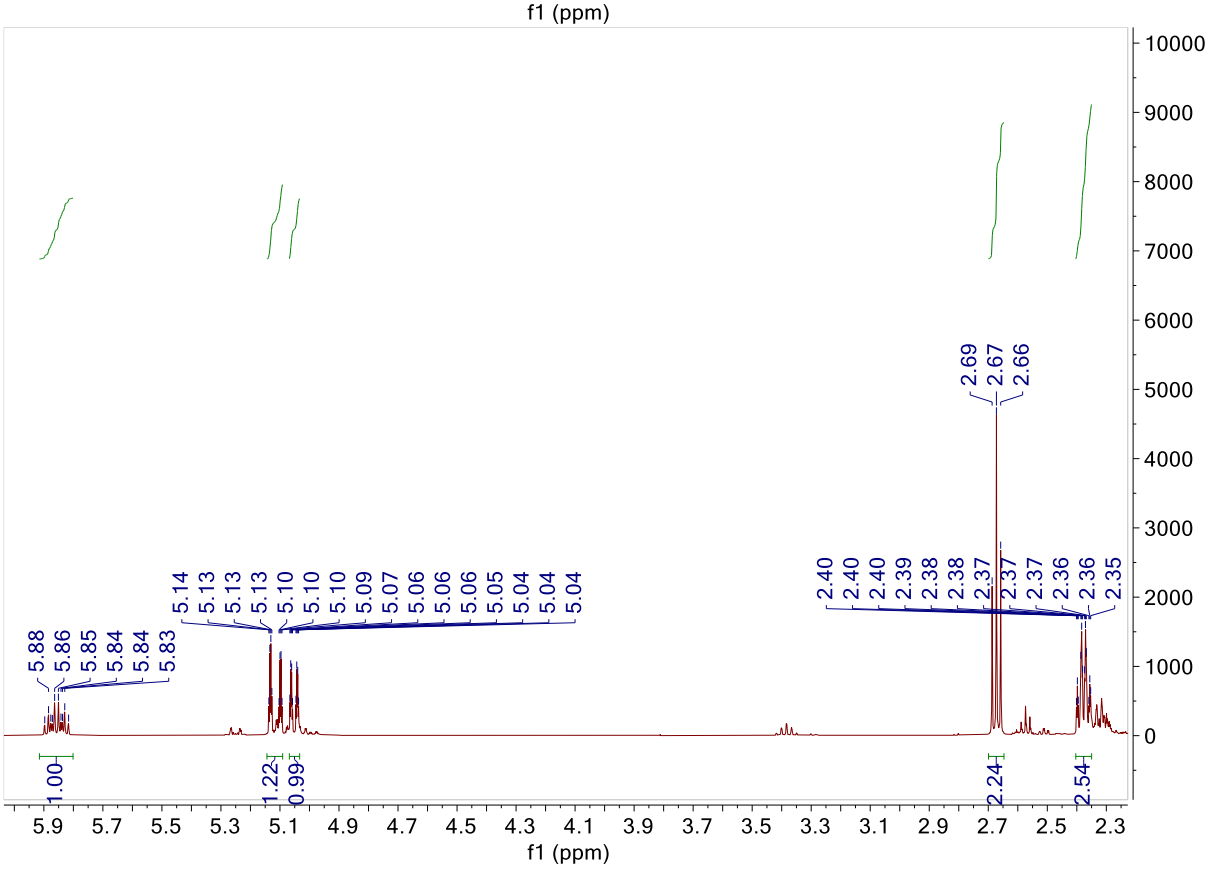
^{1}H and ^{13}C NMR data for 5a.

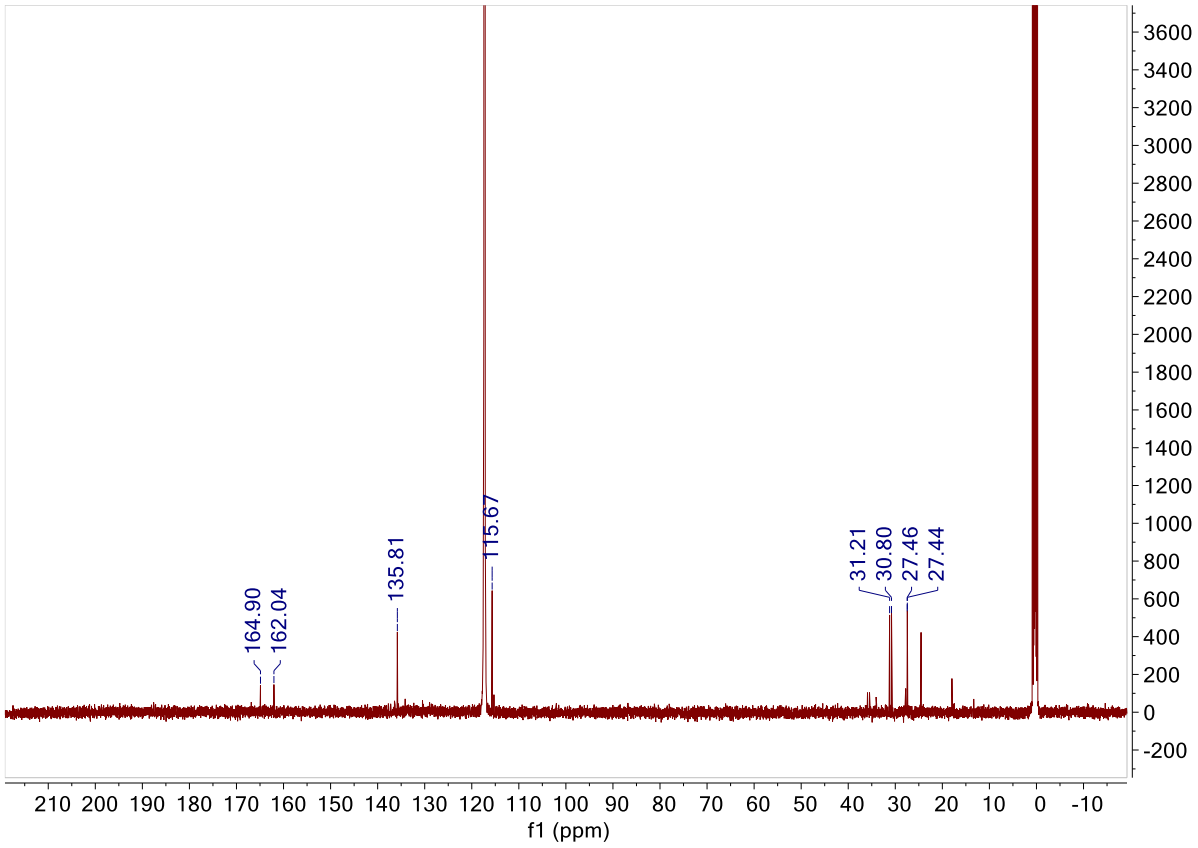




***In situ* ^{1}H, ^{13}C, and ^{19}F NMR data for 1b.**



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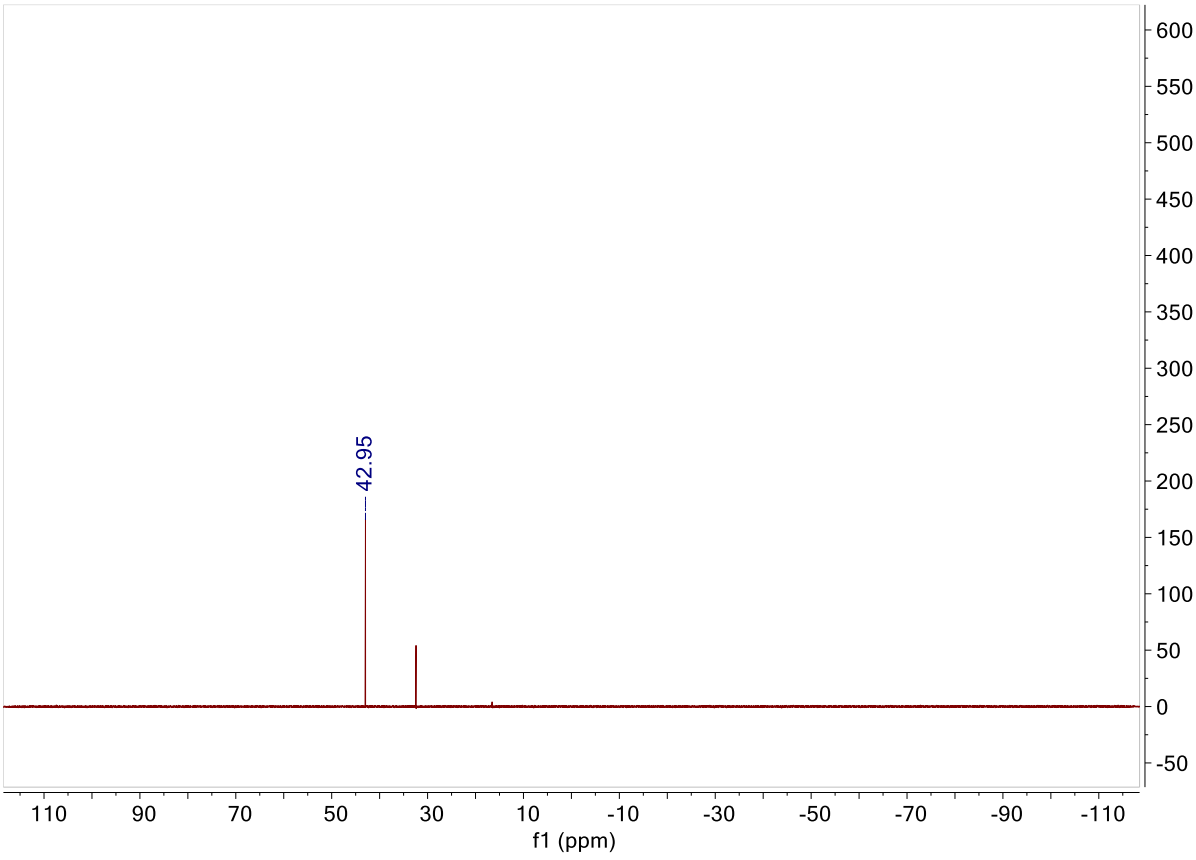
27.44
f1 (ppm)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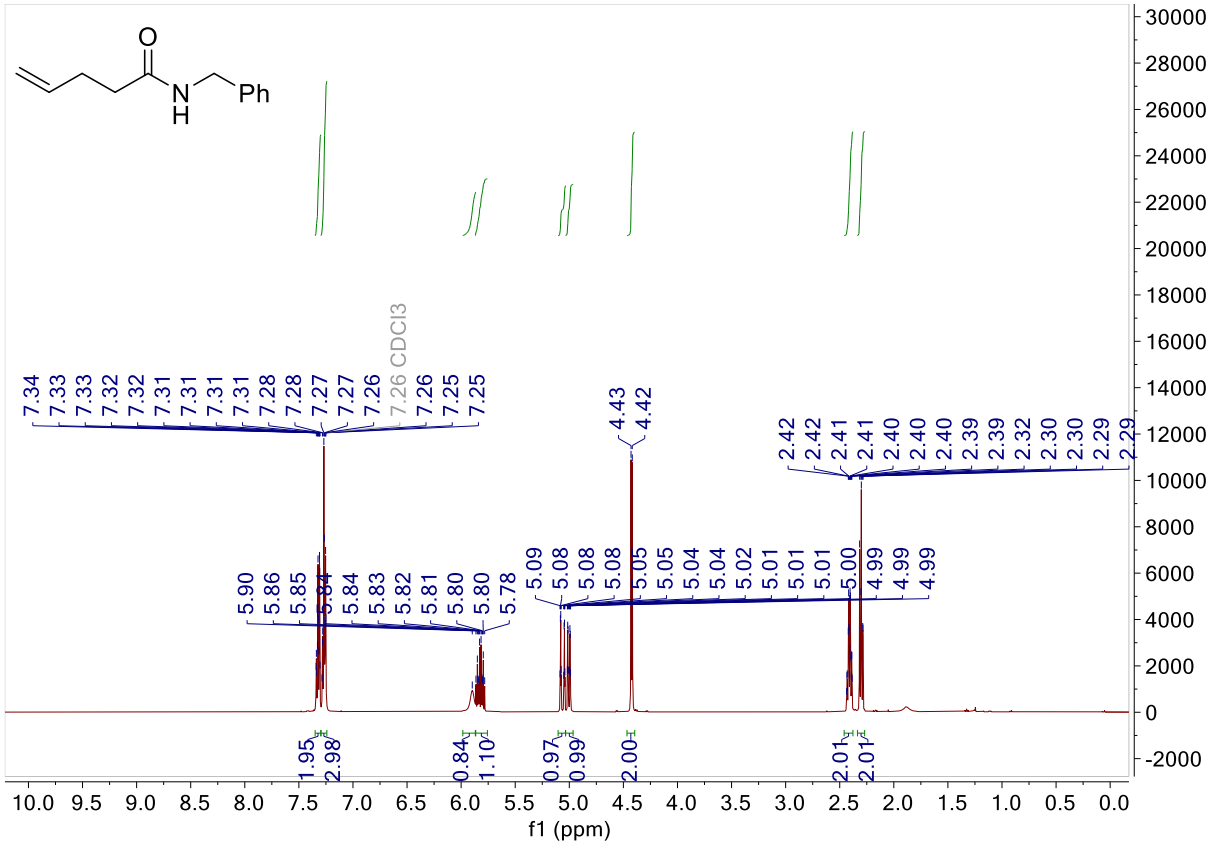
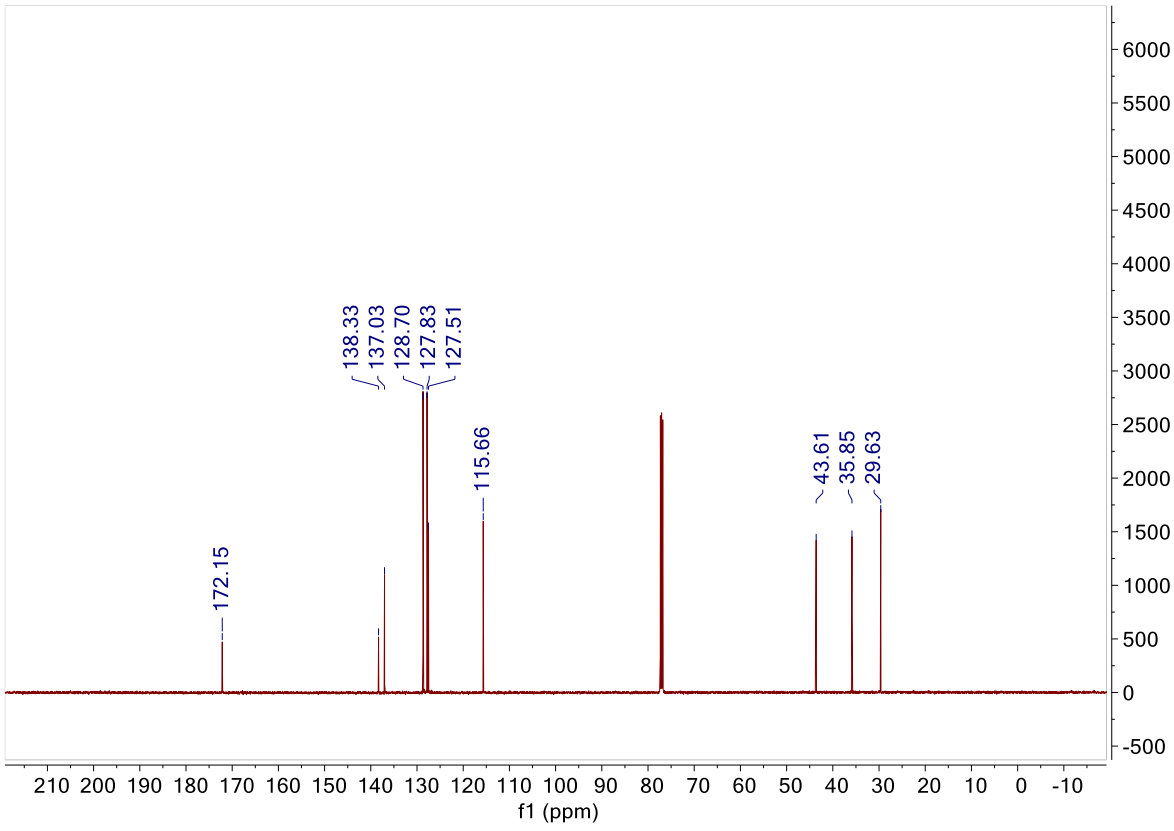
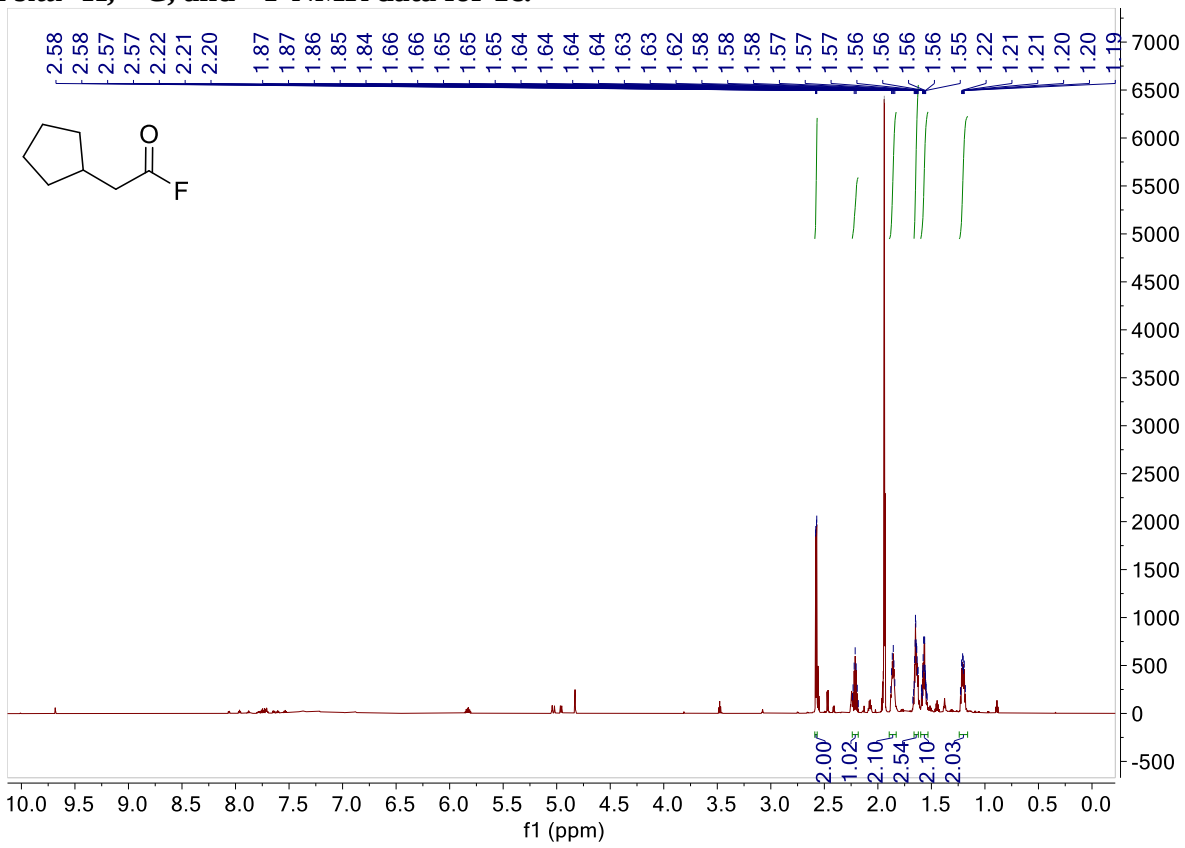
f1 (ppm)

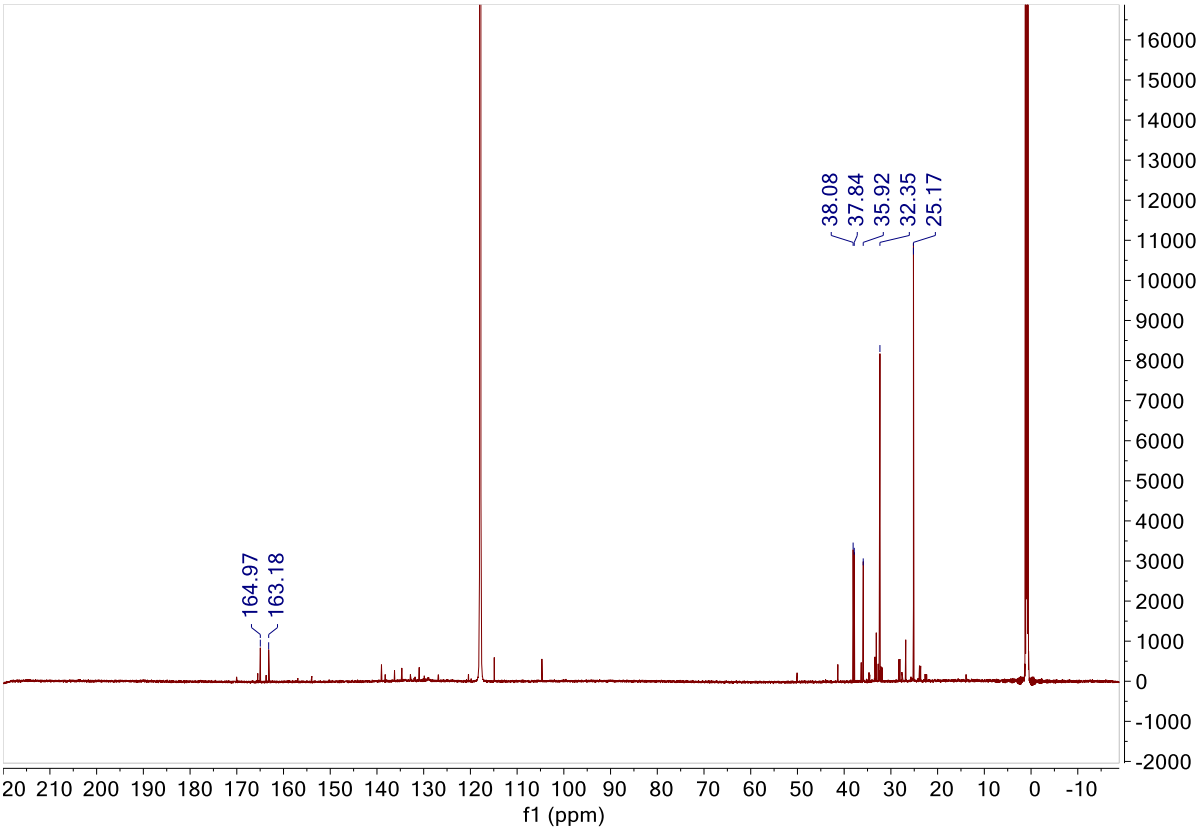
^{1}H and ^{13}C NMR data for 5b.

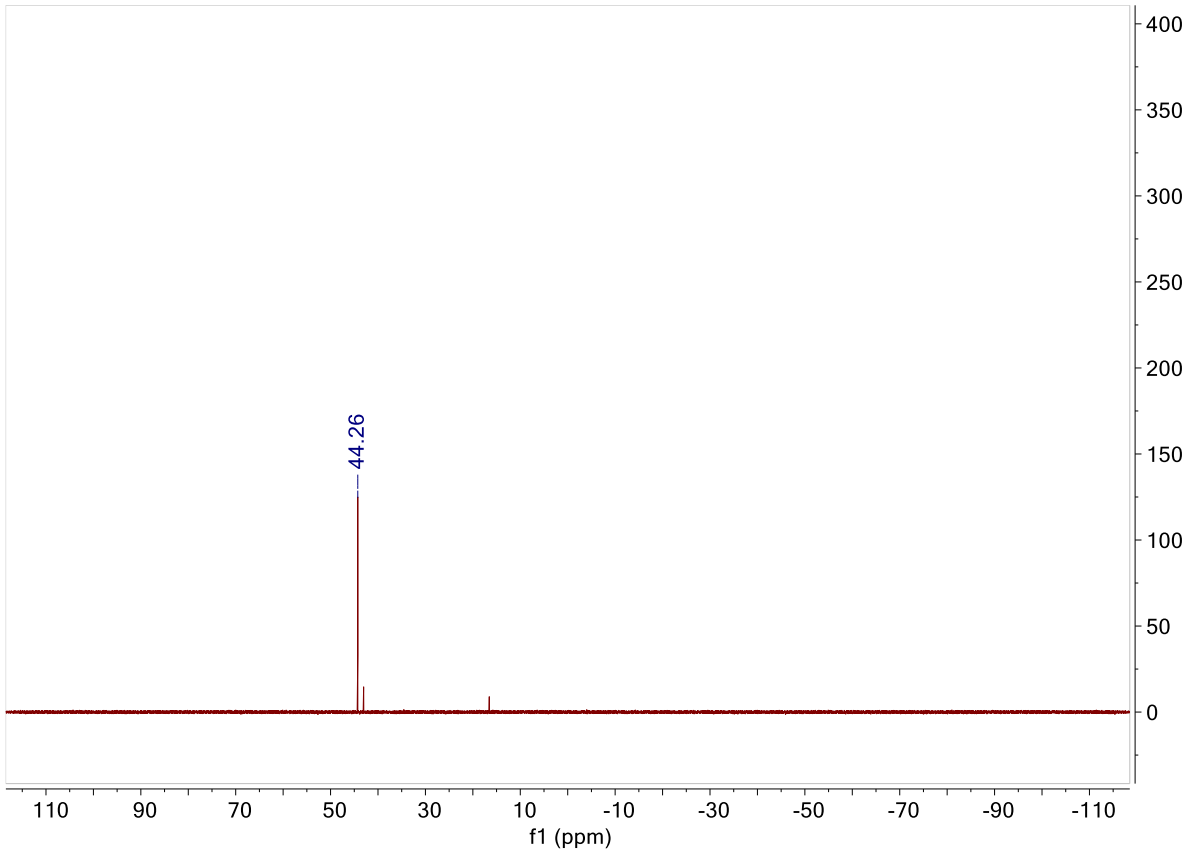




***In situ* ^{1}H, ^{13}C, and ^{19}F NMR data for 1c.**



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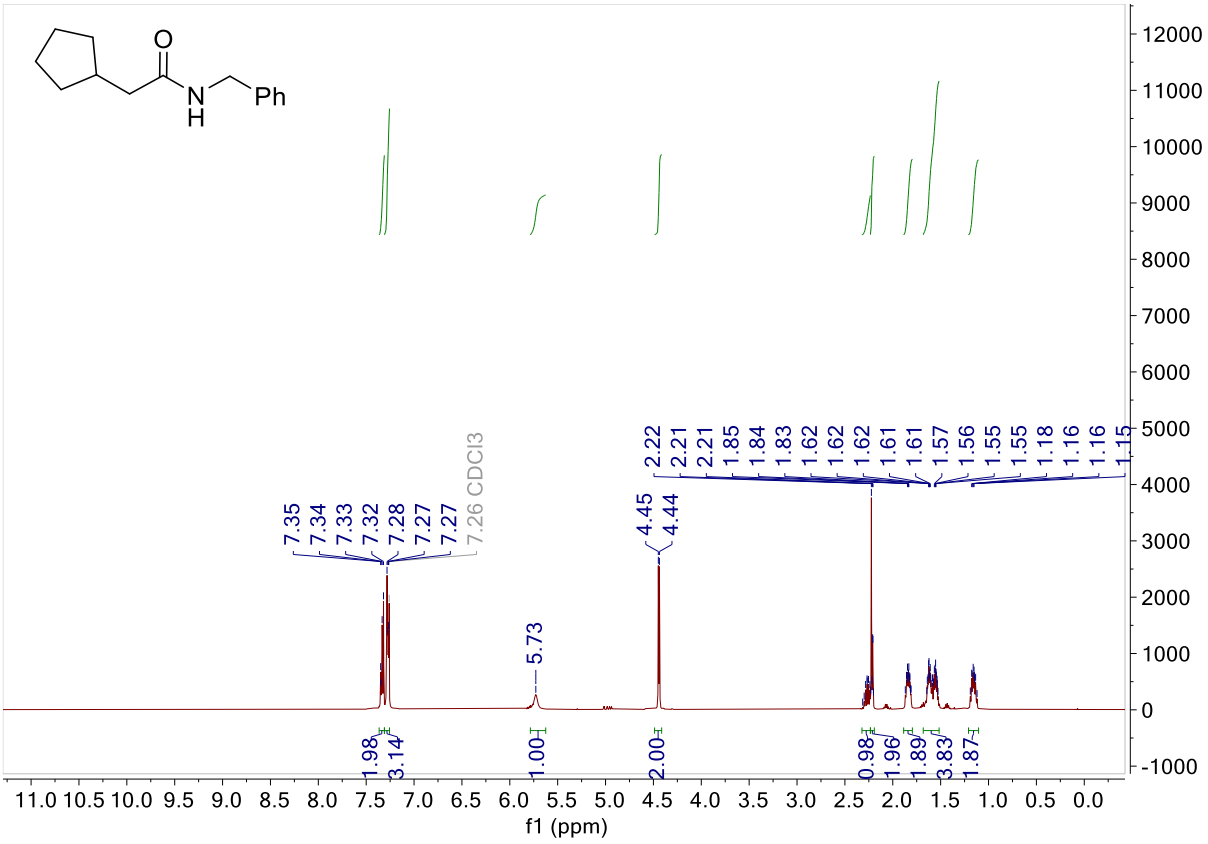
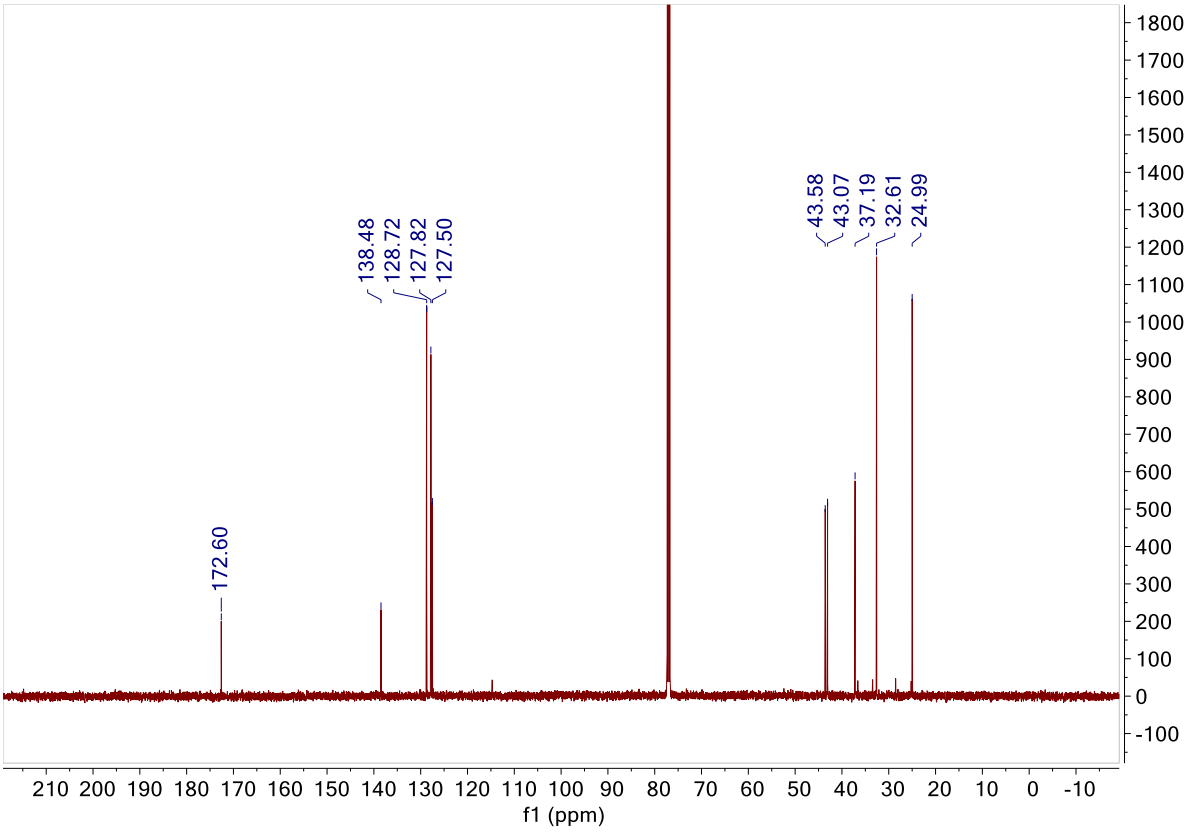
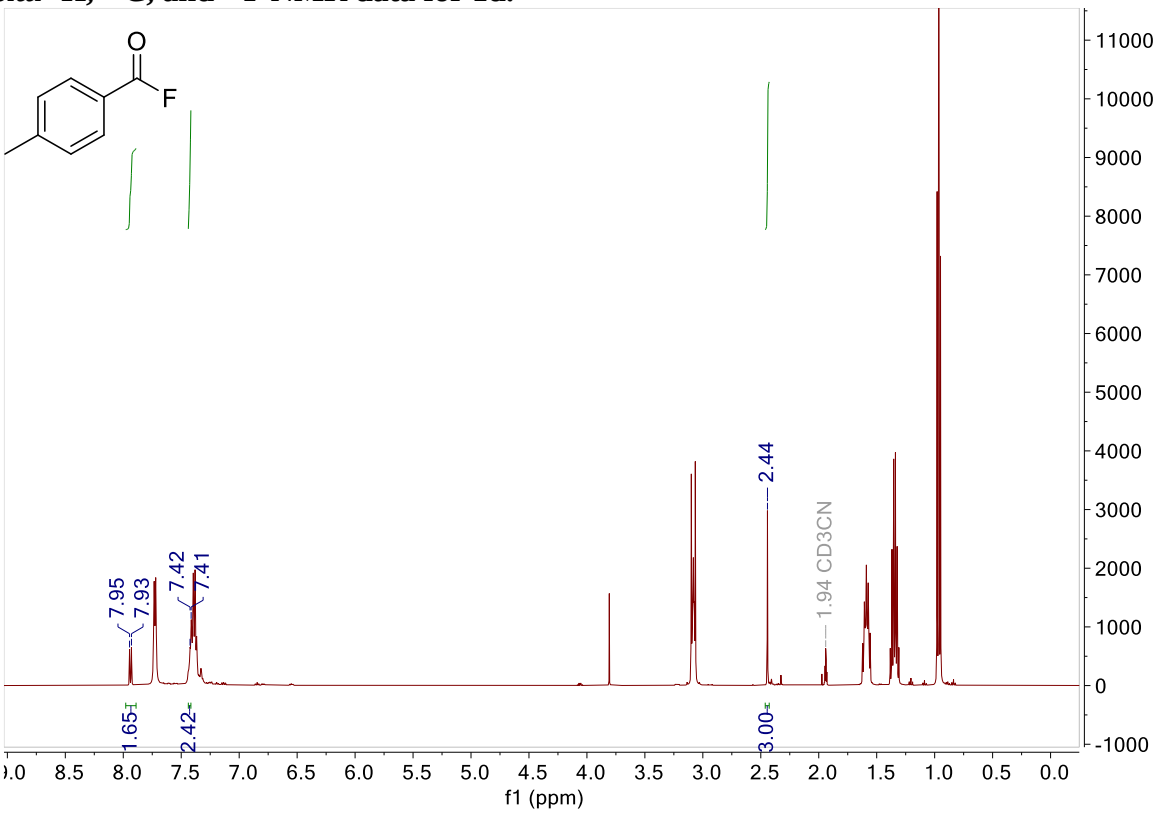
-50
-70
-90
-110
f1 (ppm)

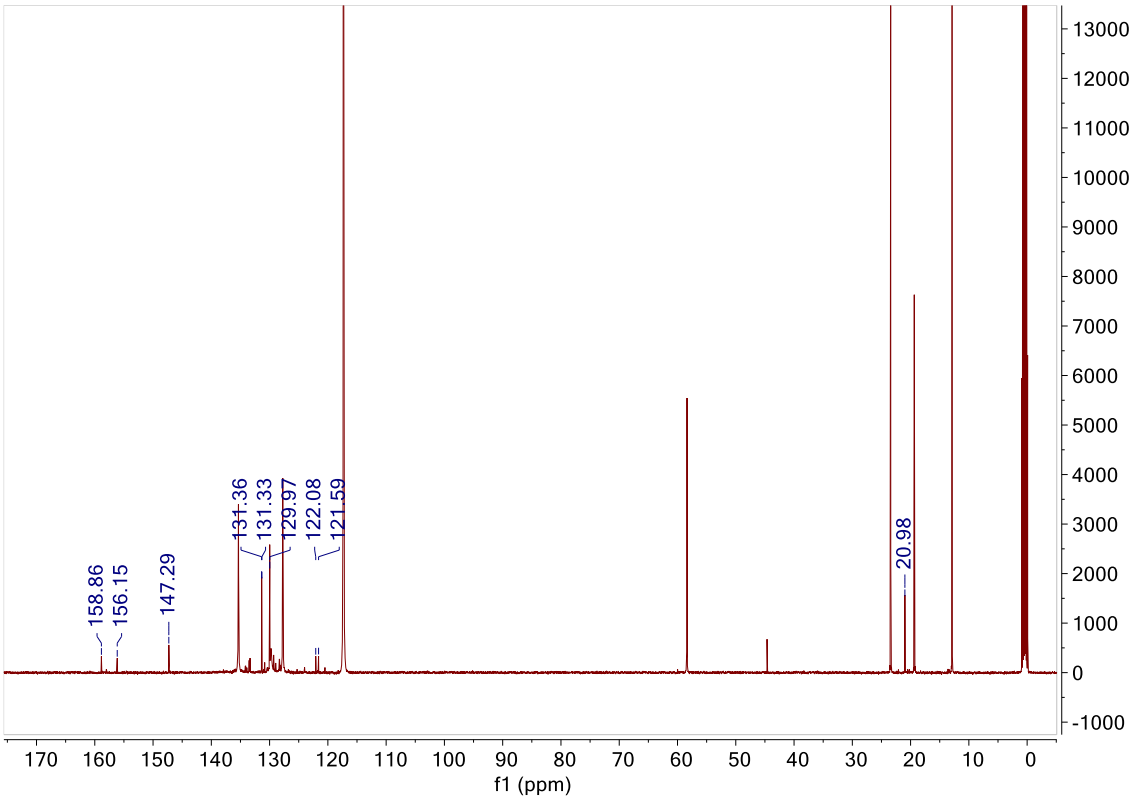
^{1}H and ^{13}C NMR data for 5c.

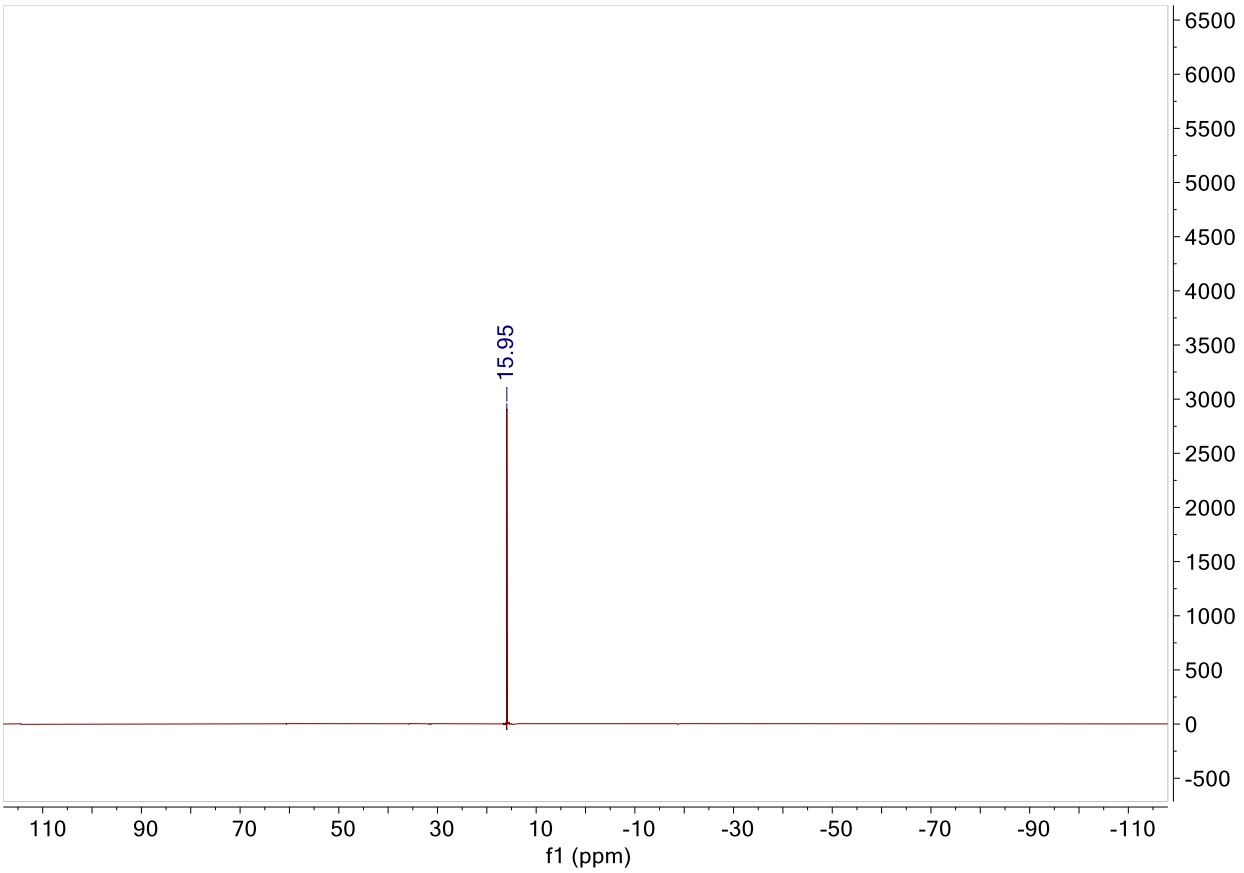




***In situ* ^{1}H, ^{13}C, and ^{19}F NMR data for 1d.**



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500
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-500
110
90
70
50
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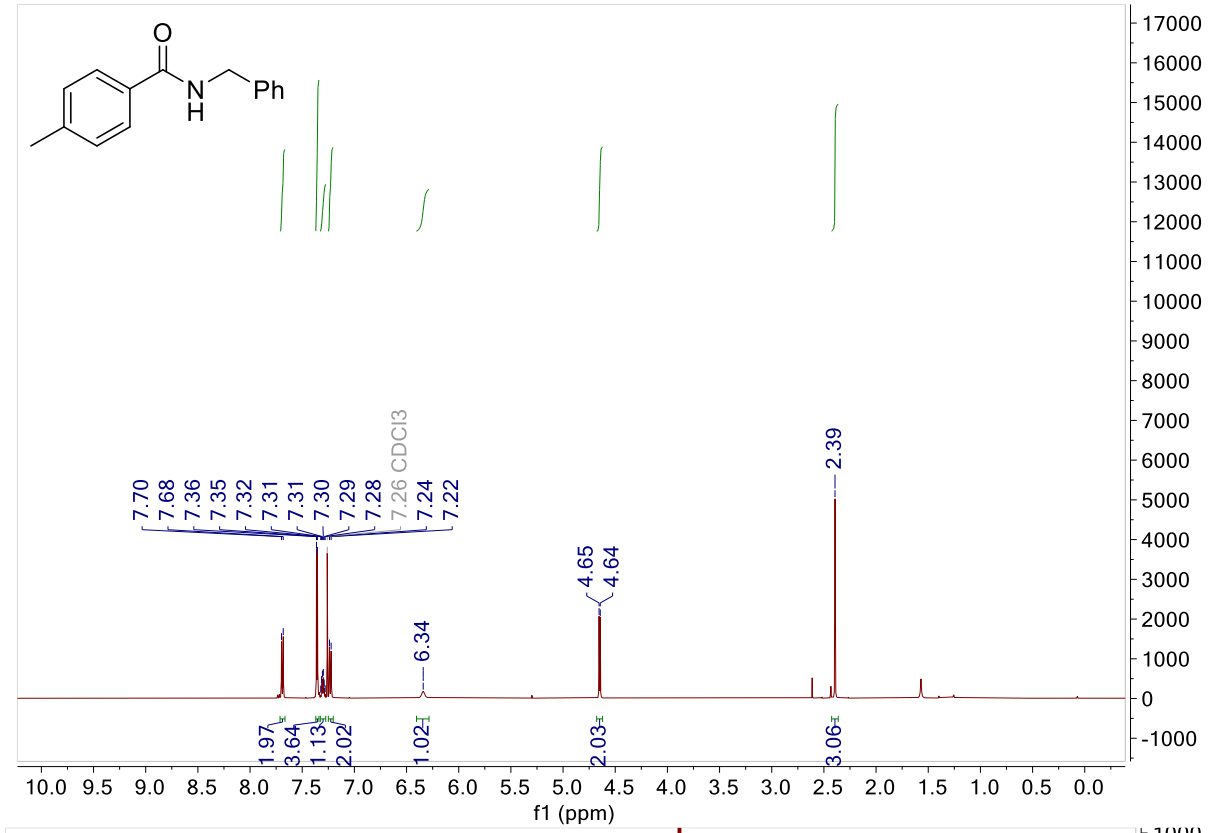
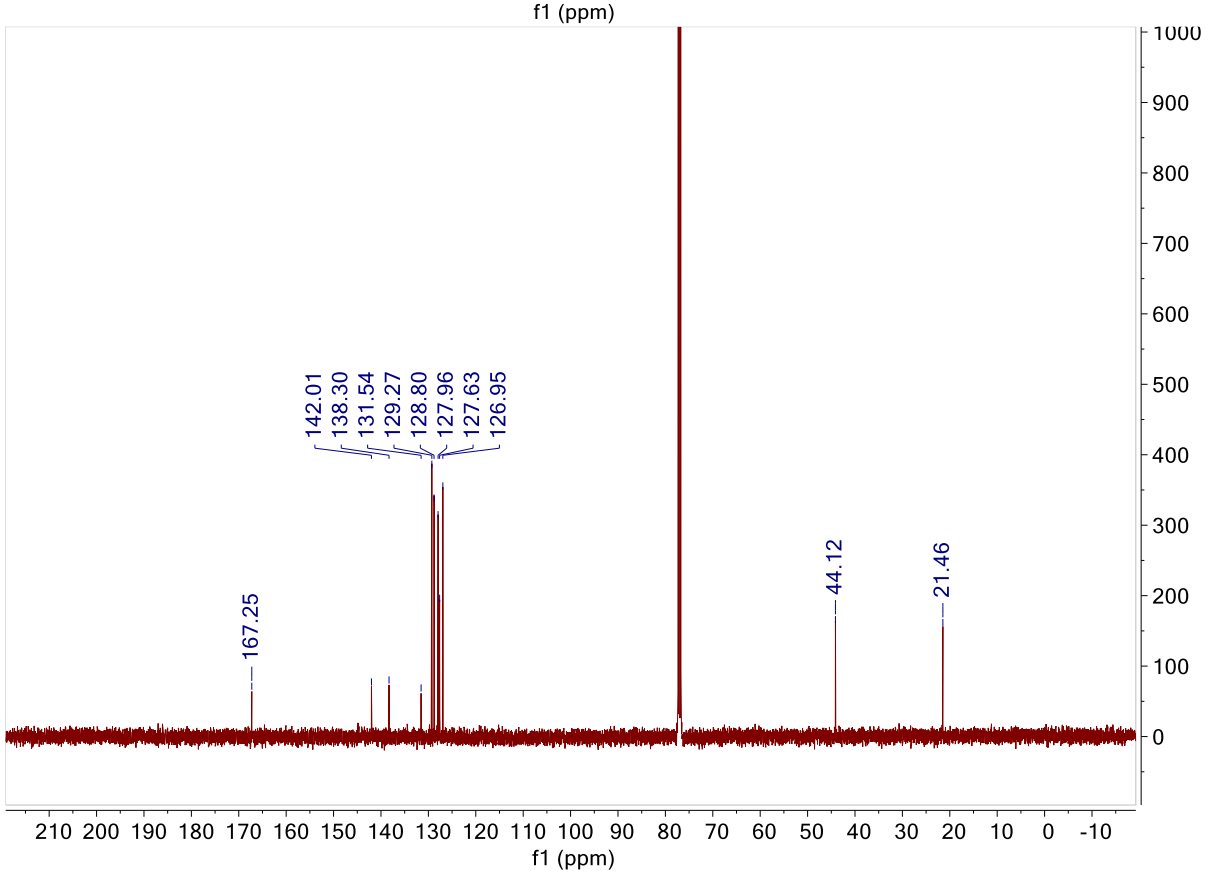
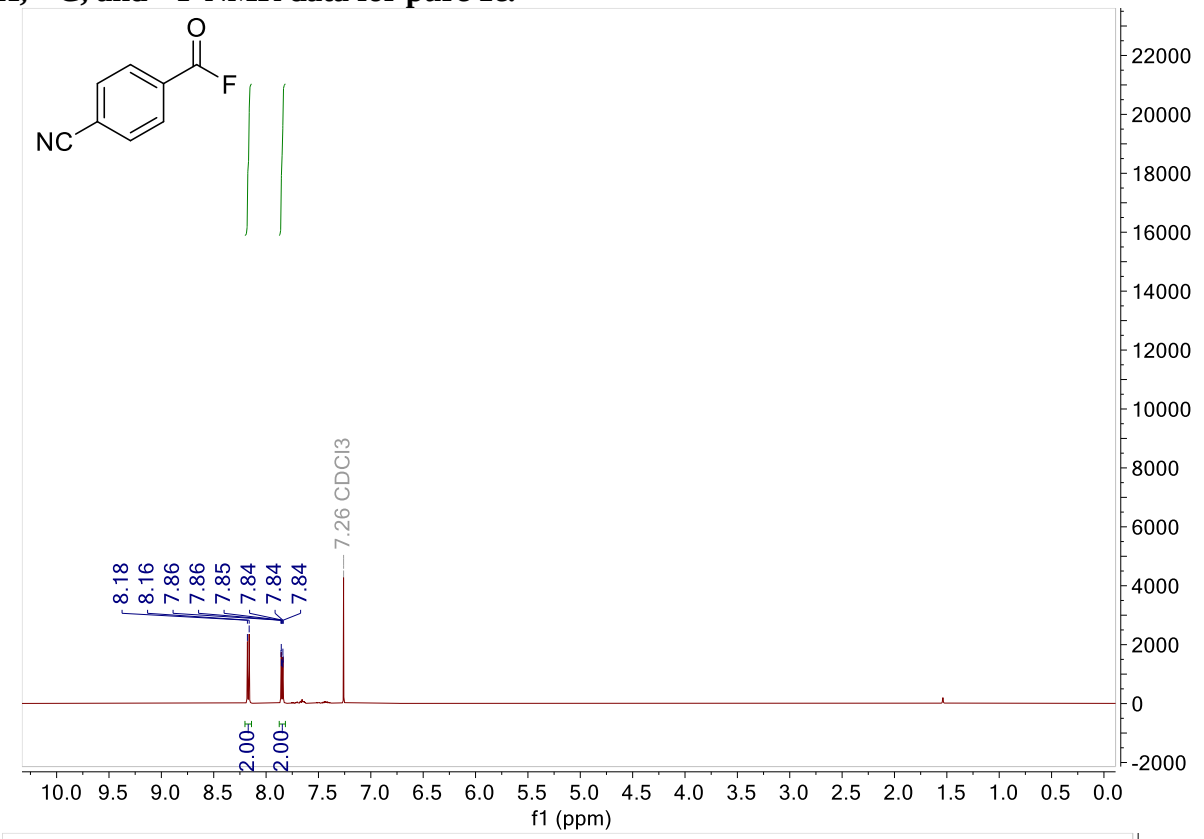
-10
-30
-50
-70
-90
-110
f1 (ppm)

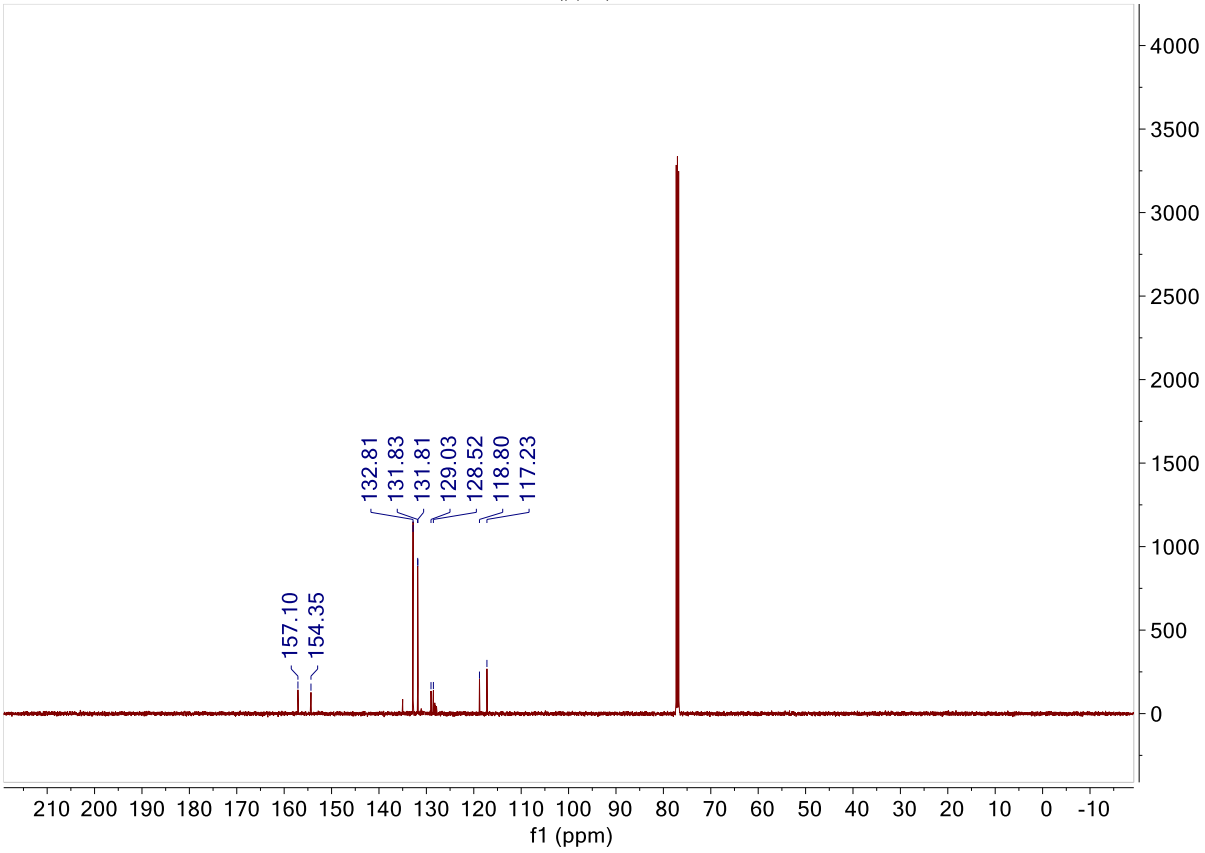
^{1}H and ^{13}C NMR data for 5d.

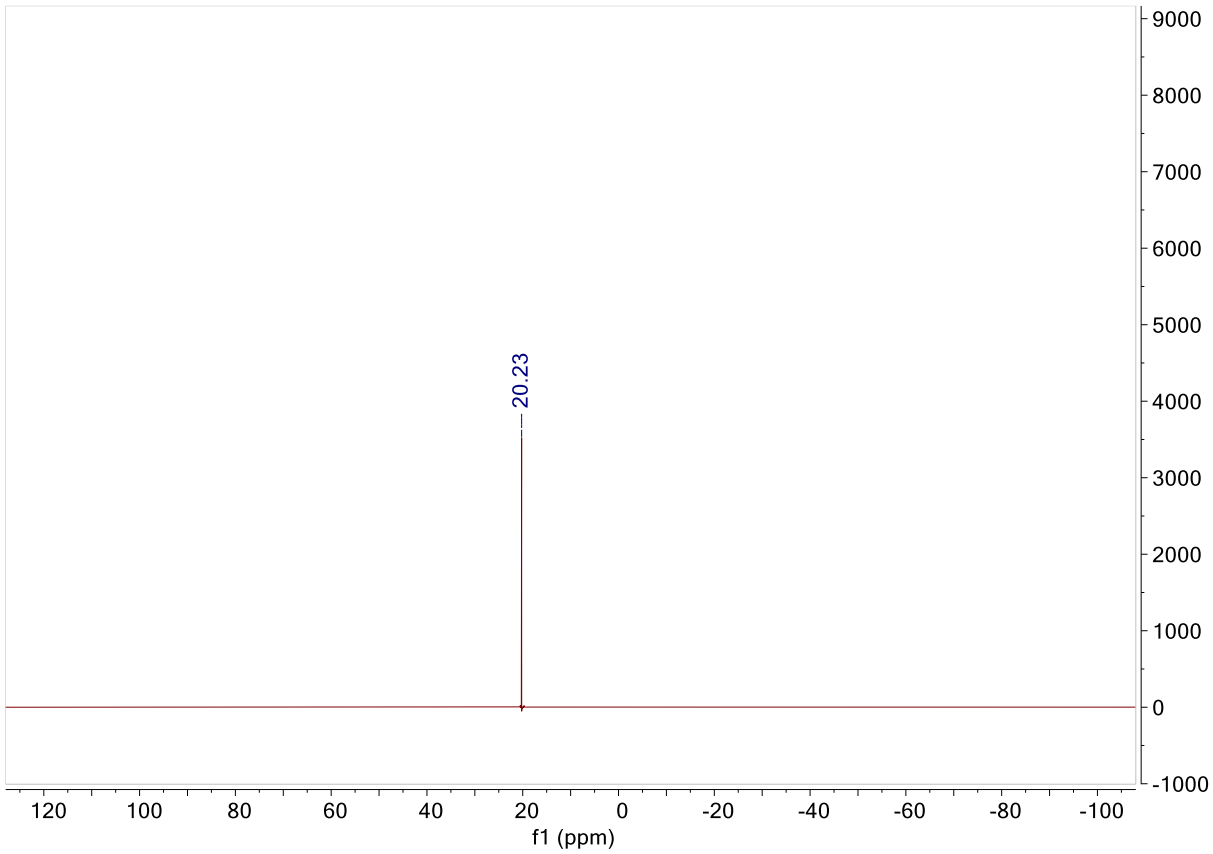




^{1}H, ^{13}C, and ^{19}F NMR data for pure 1e.



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-20
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-80
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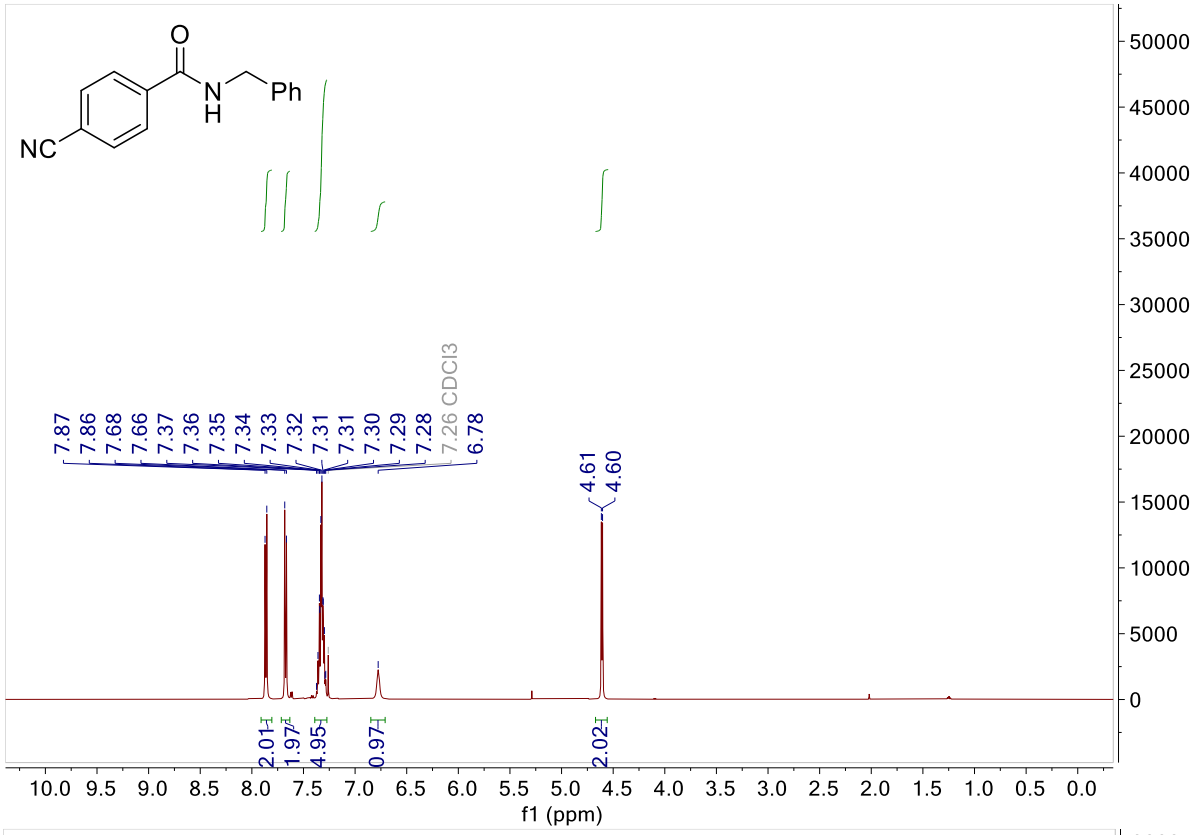
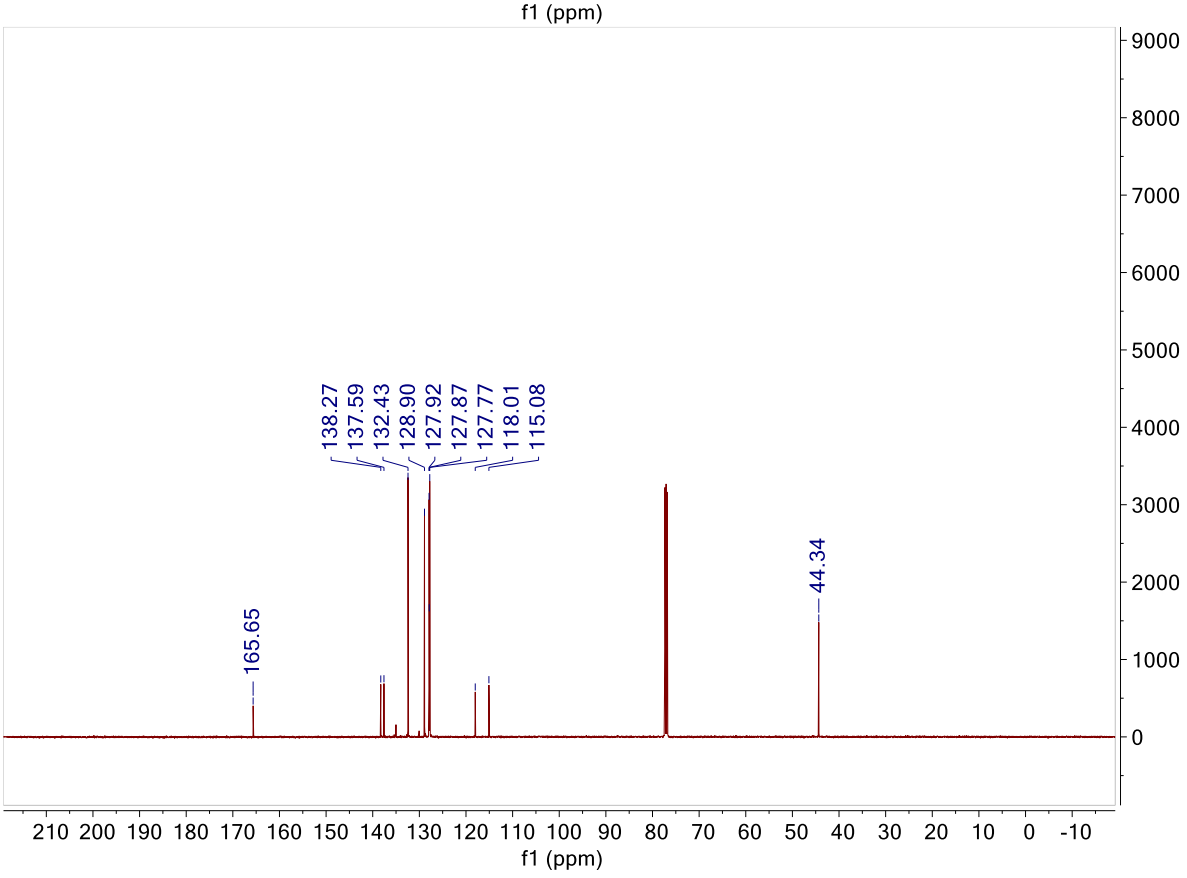
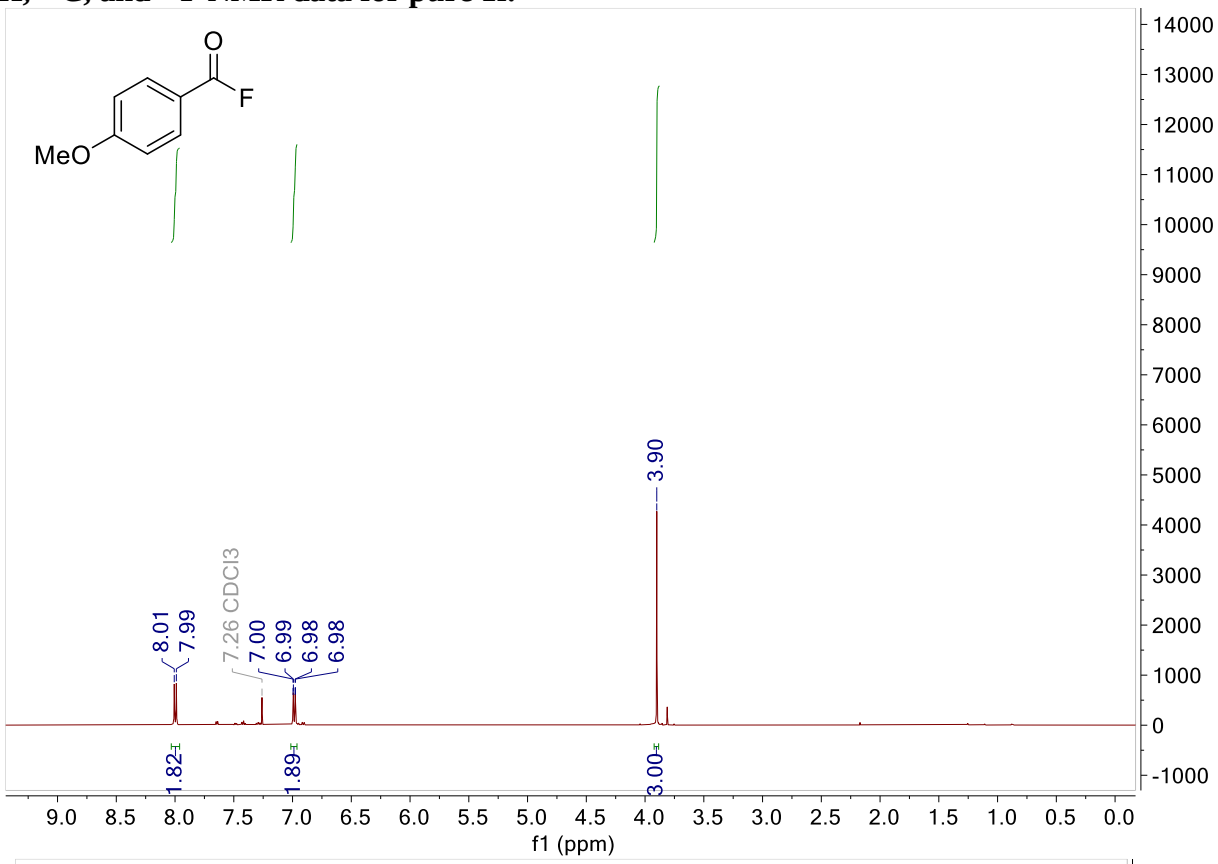
f1 (ppm)

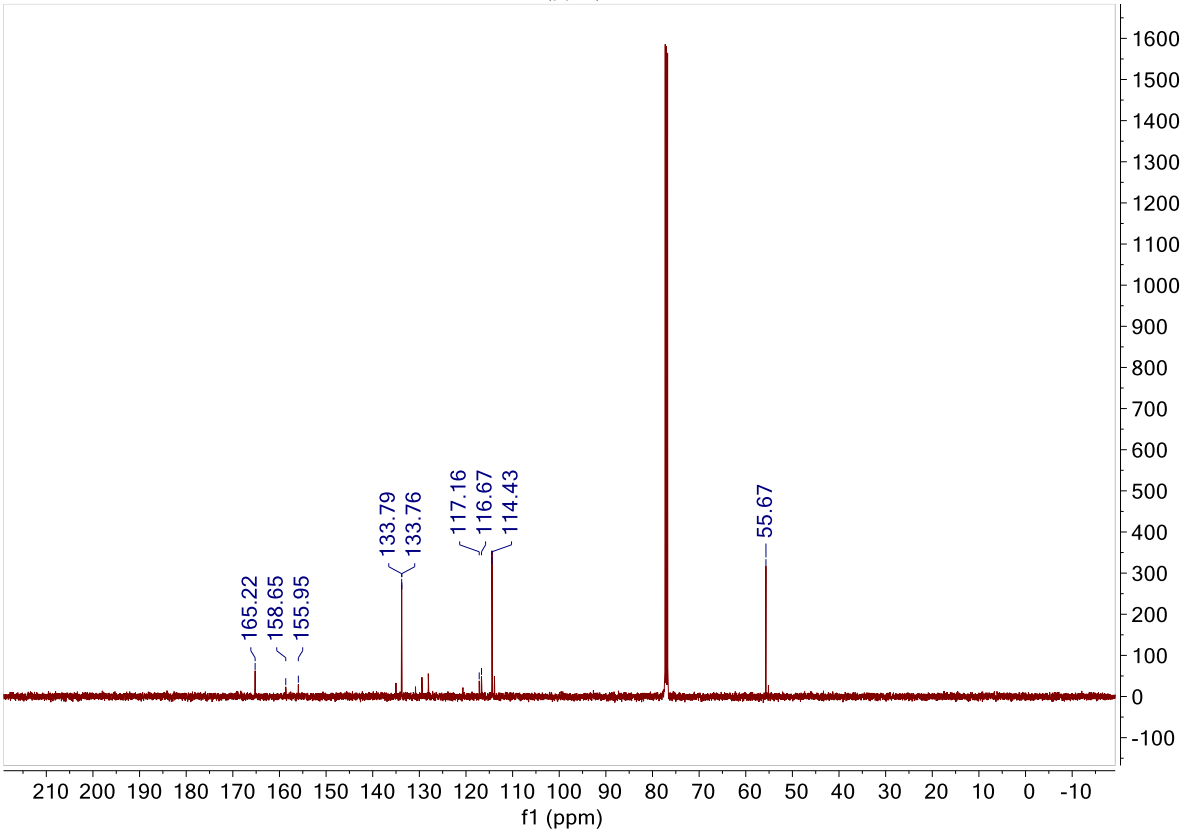
^{1}H and ^{13}C NMR data for 5e.

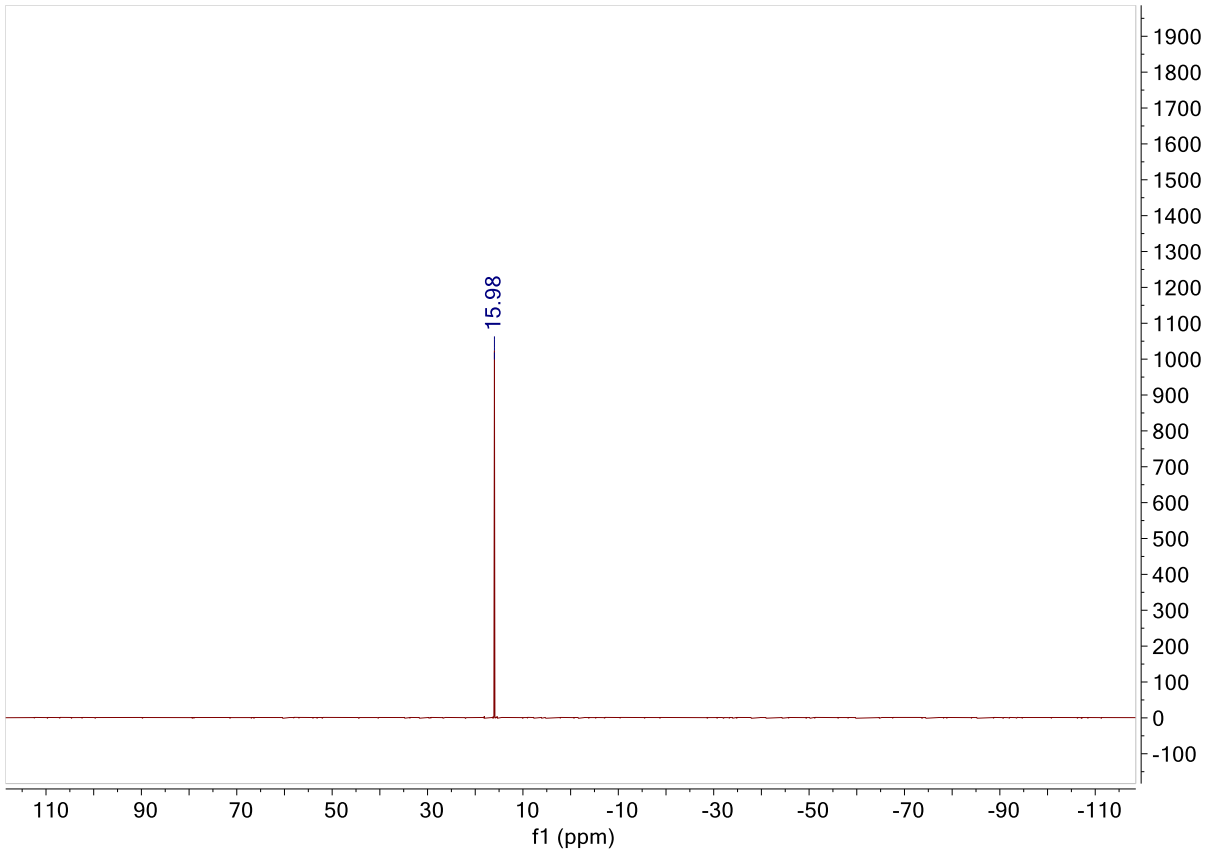




^{1}H, ^{13}C, and ^{19}F NMR data for pure 1f.



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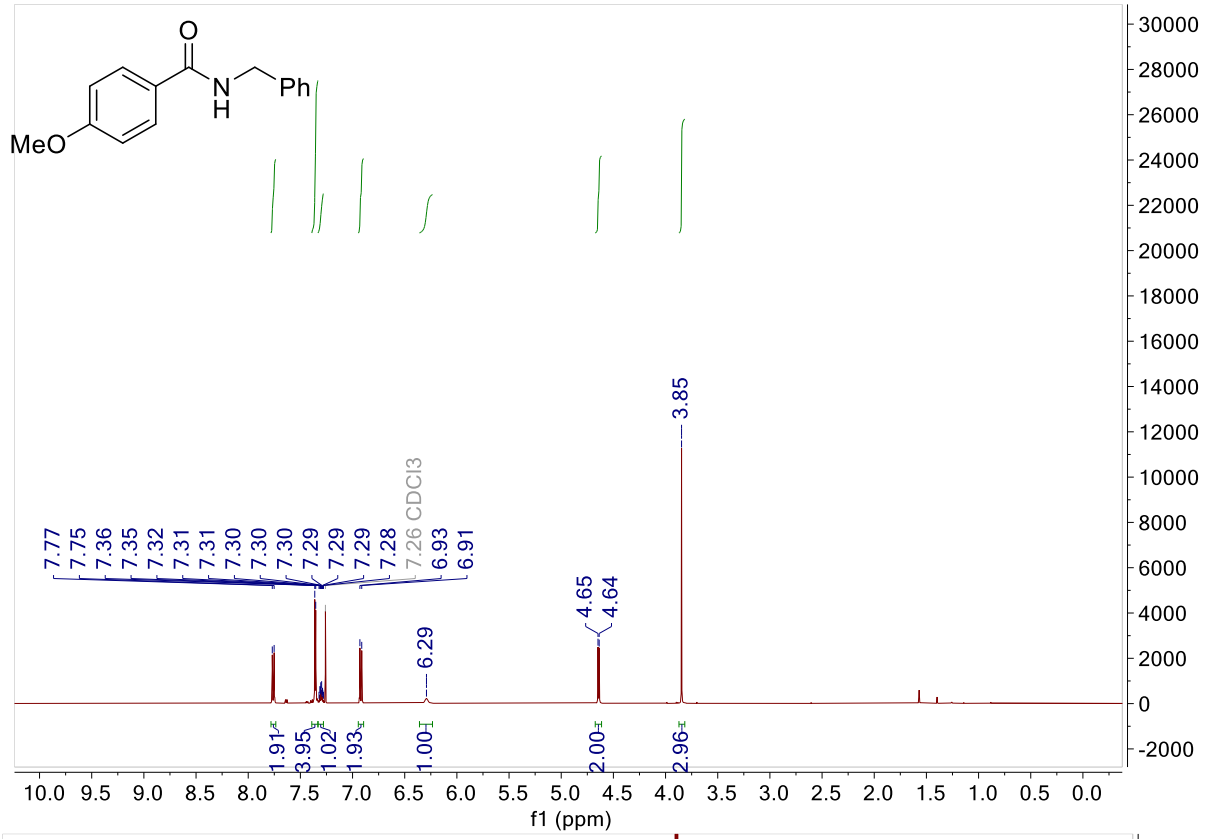
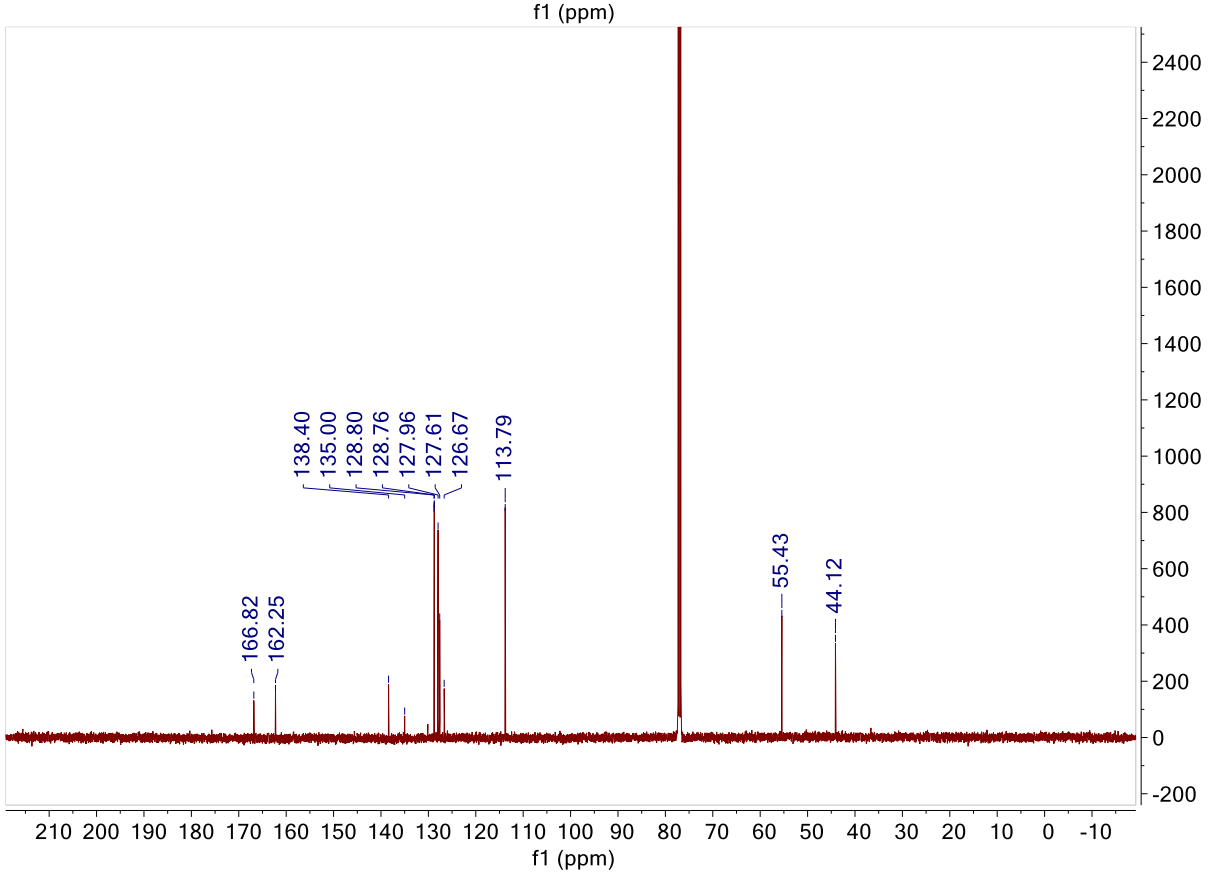
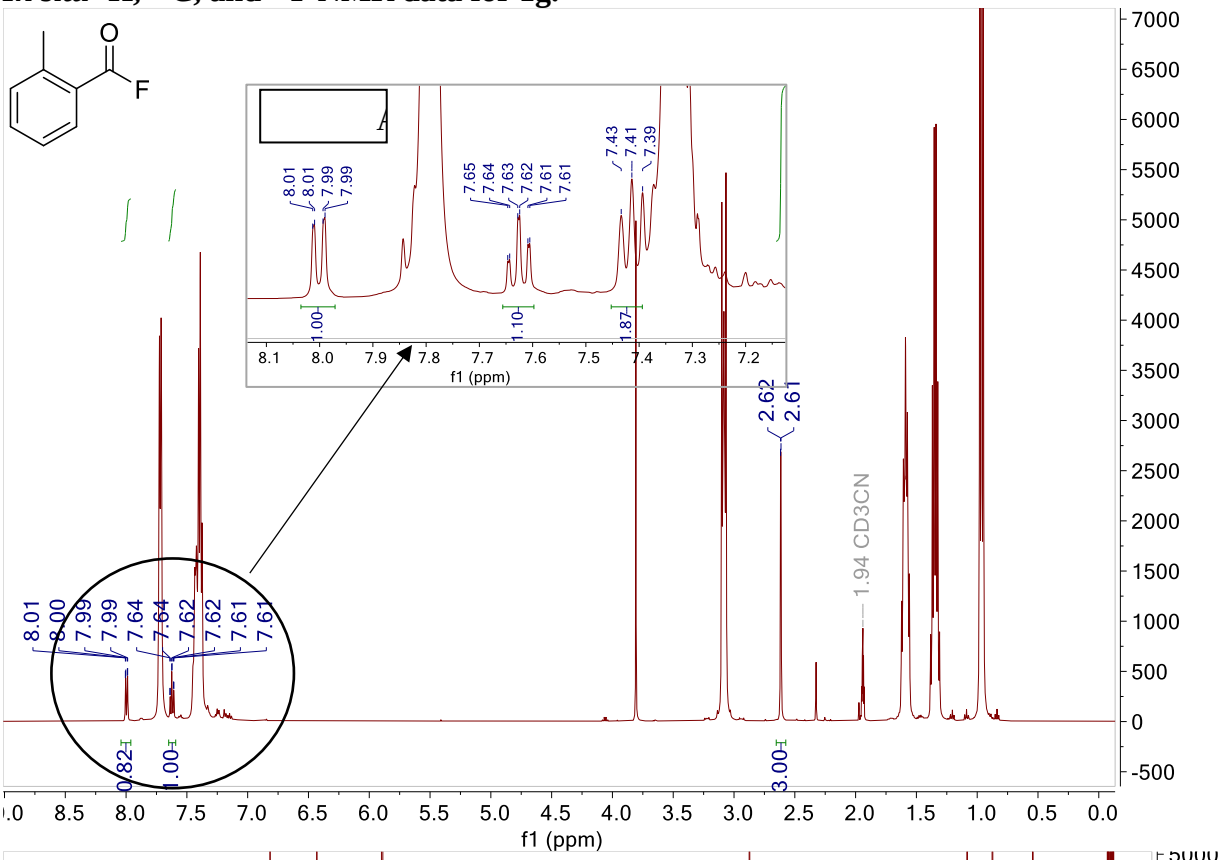
f1 (ppm)

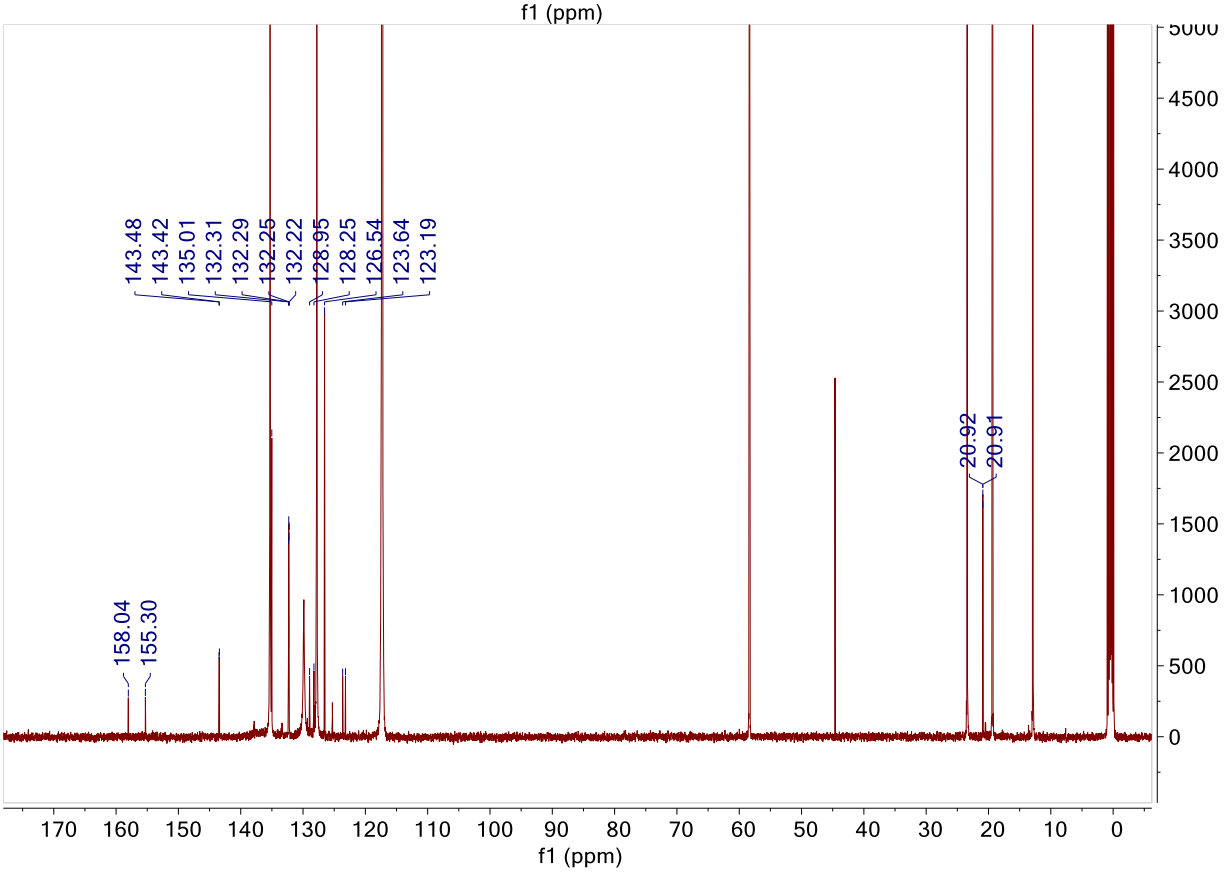
^{1}H and ^{13}C NMR data for 5f.

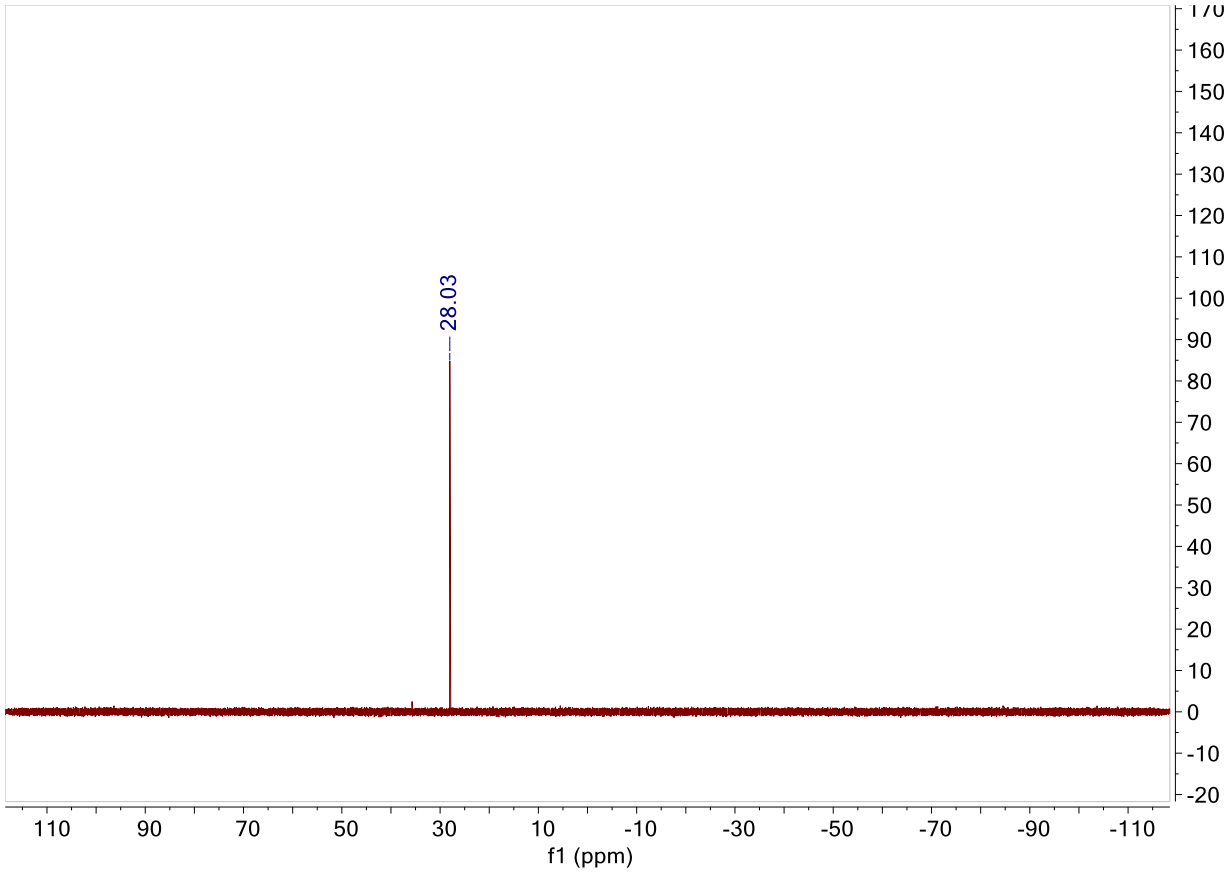




***In situ* ^{1}H, ^{13}C, and ^{19}F NMR data for 1g.**



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110
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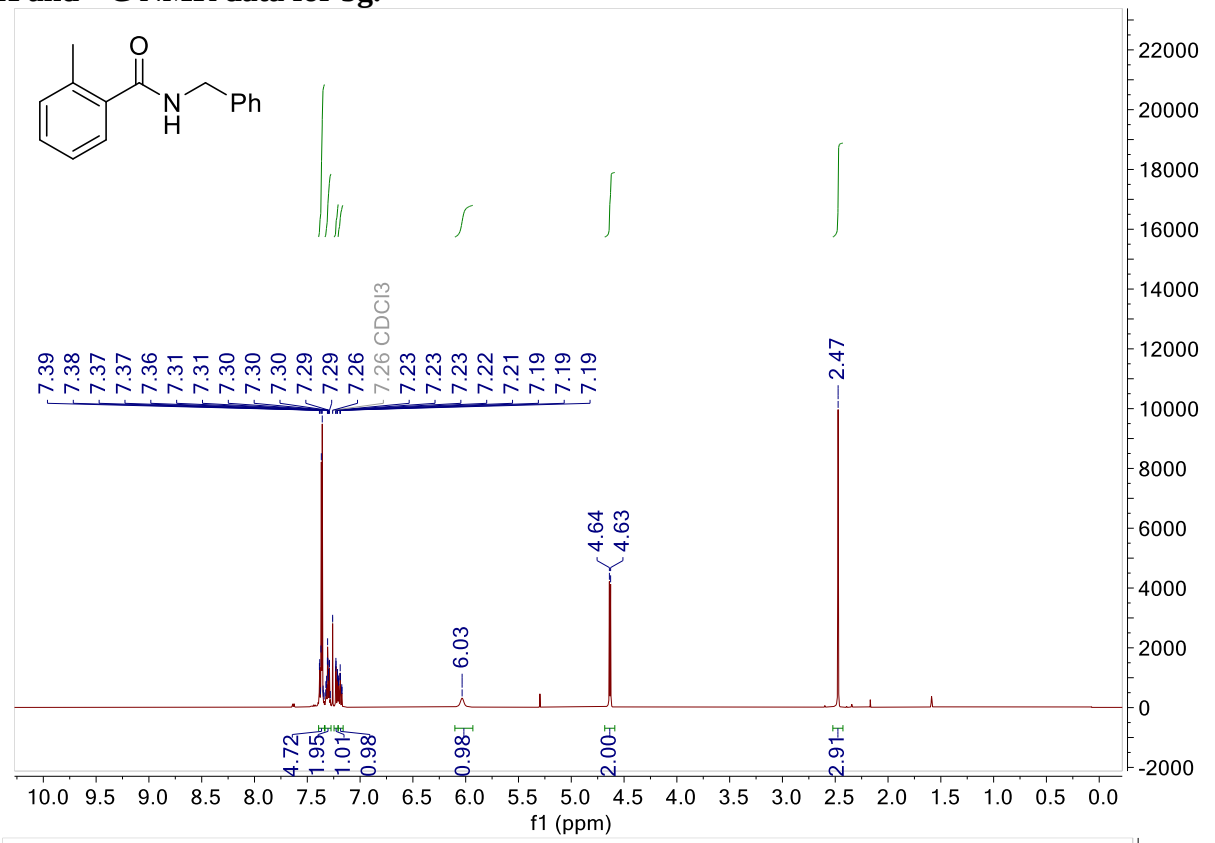
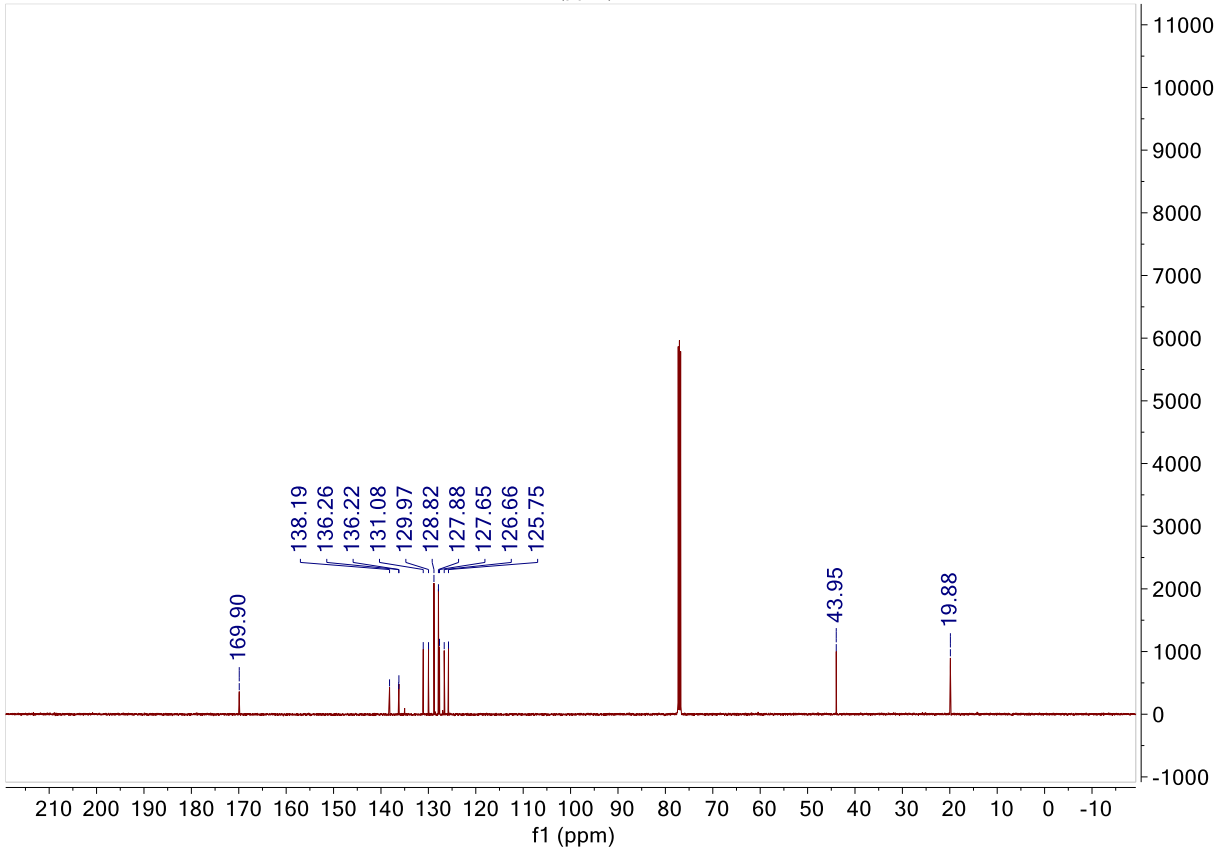
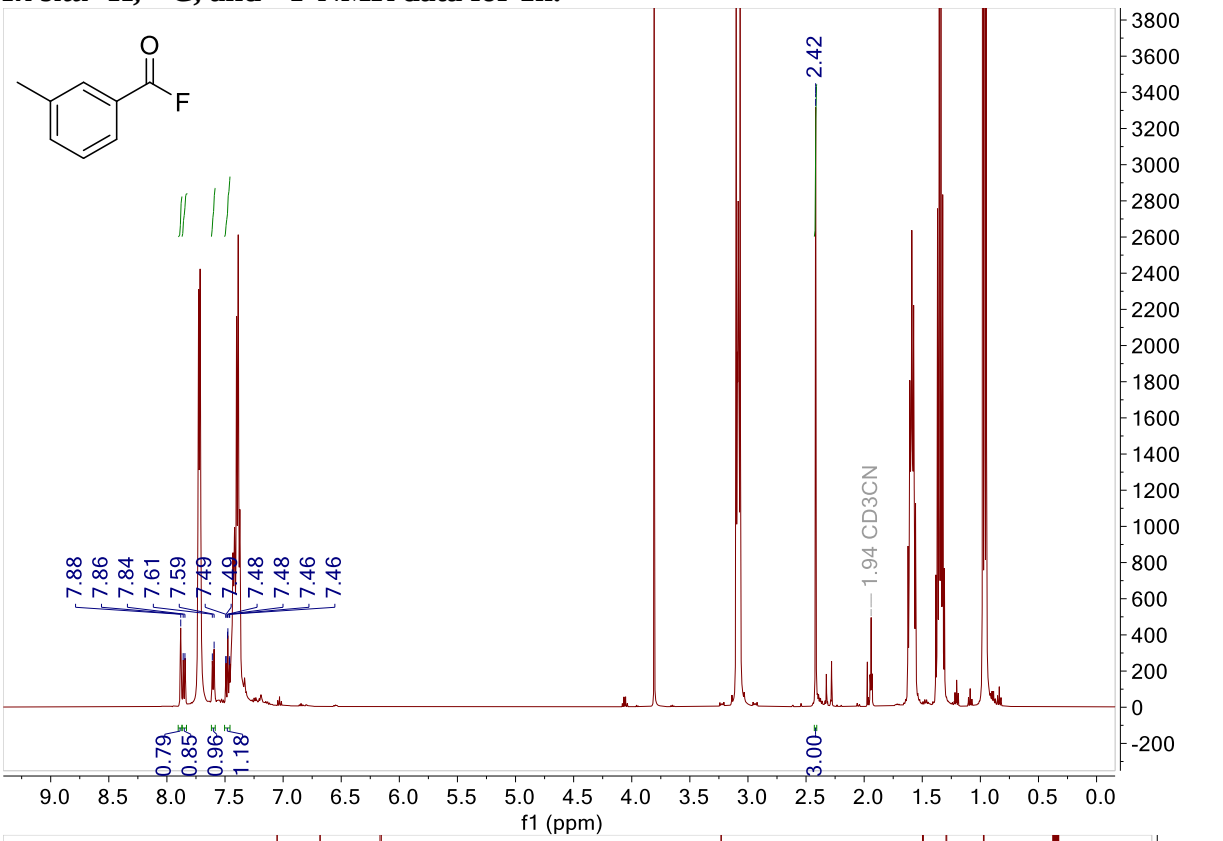
f1 (ppm)

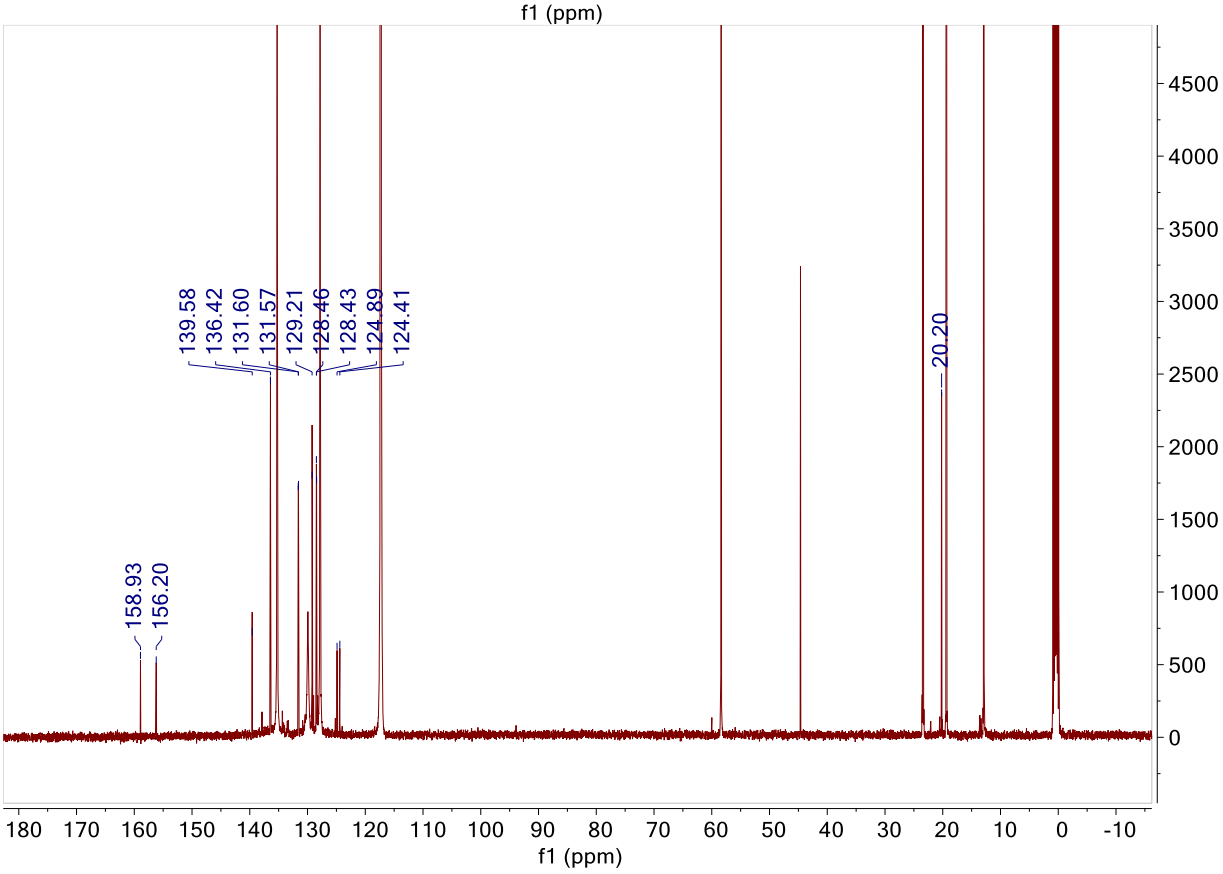
^{1}H and ^{13}C NMR data for 5g.

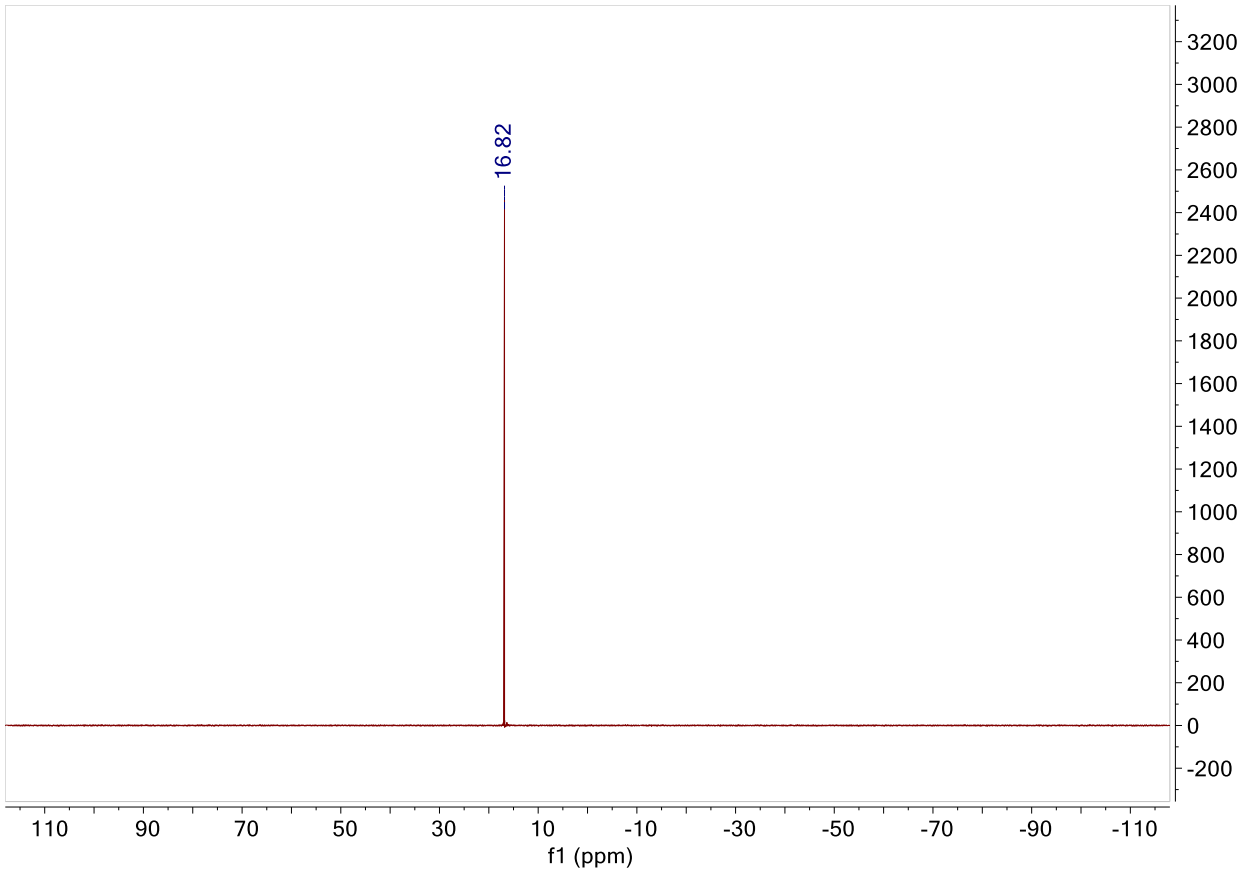




***In situ* ^{1}H, ^{13}C, and ^{19}F NMR data for 1h.**



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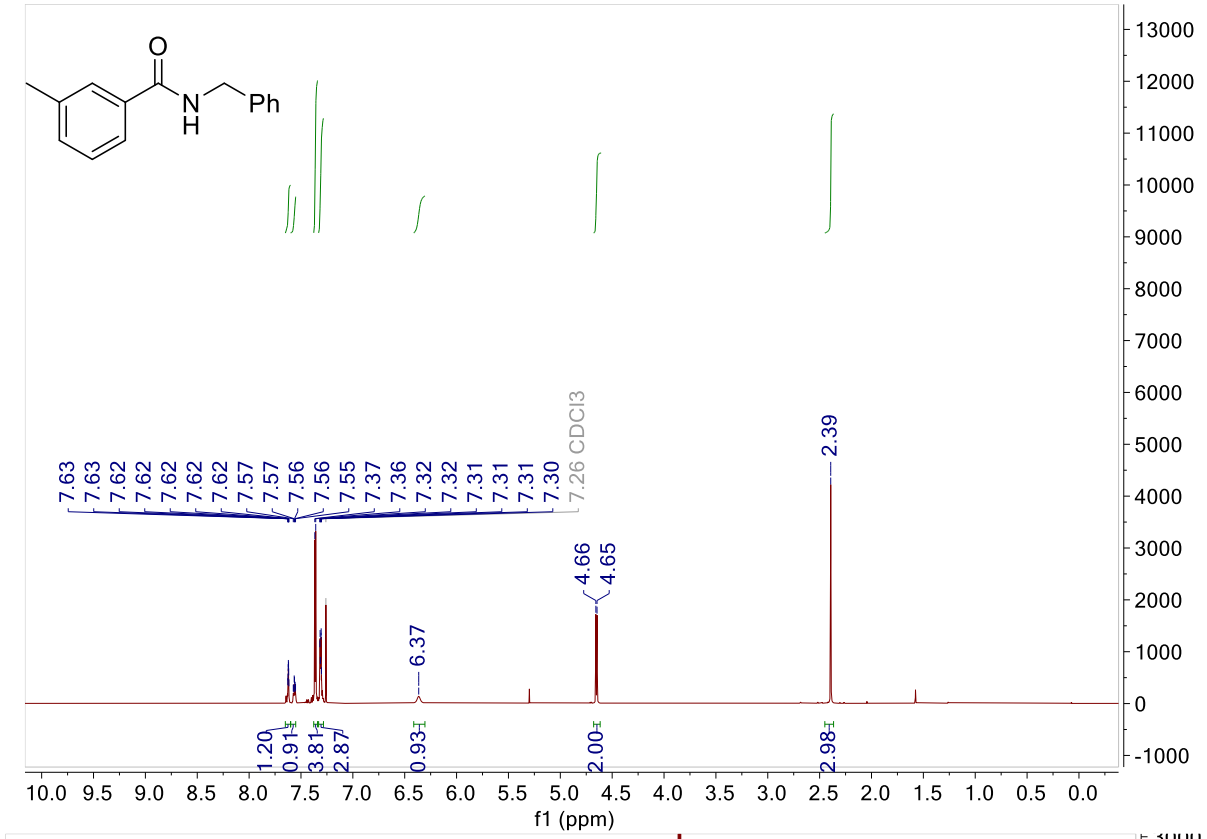
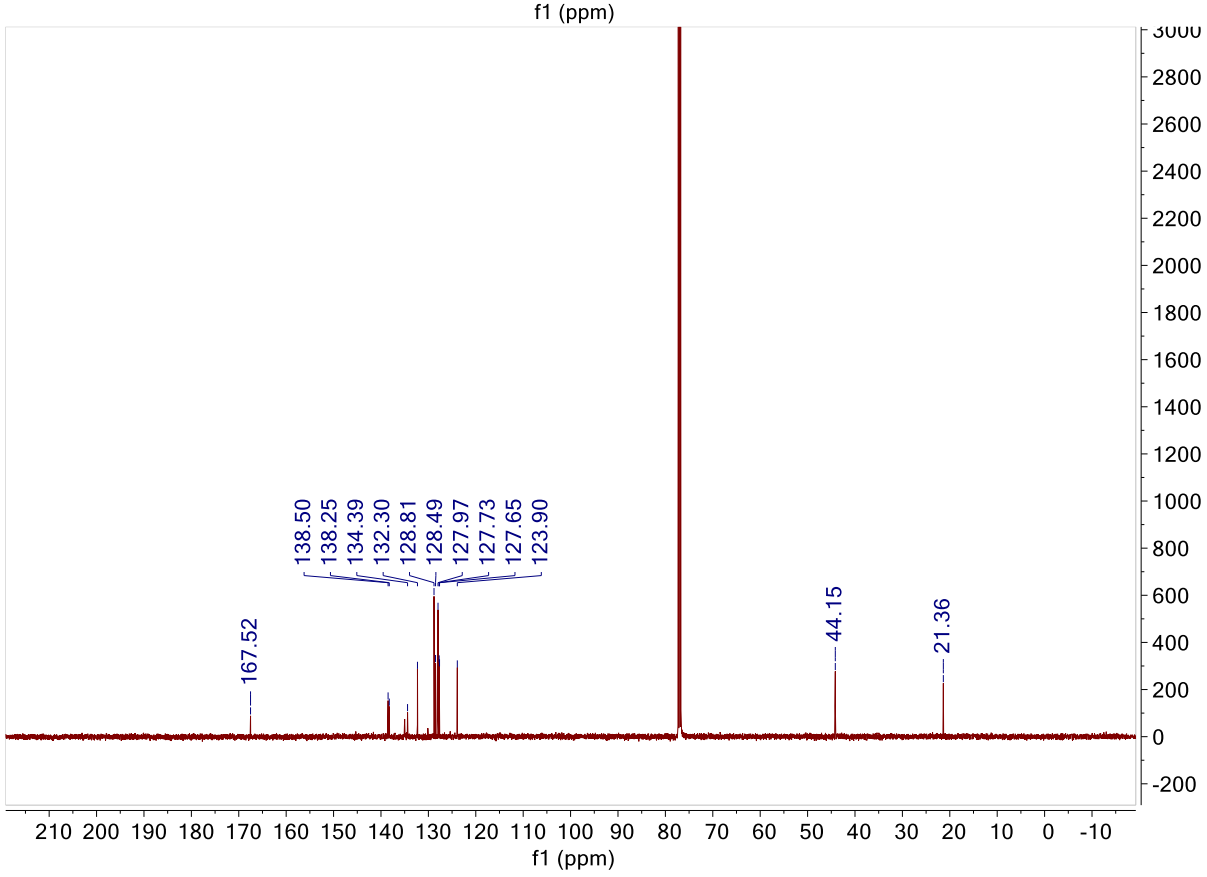
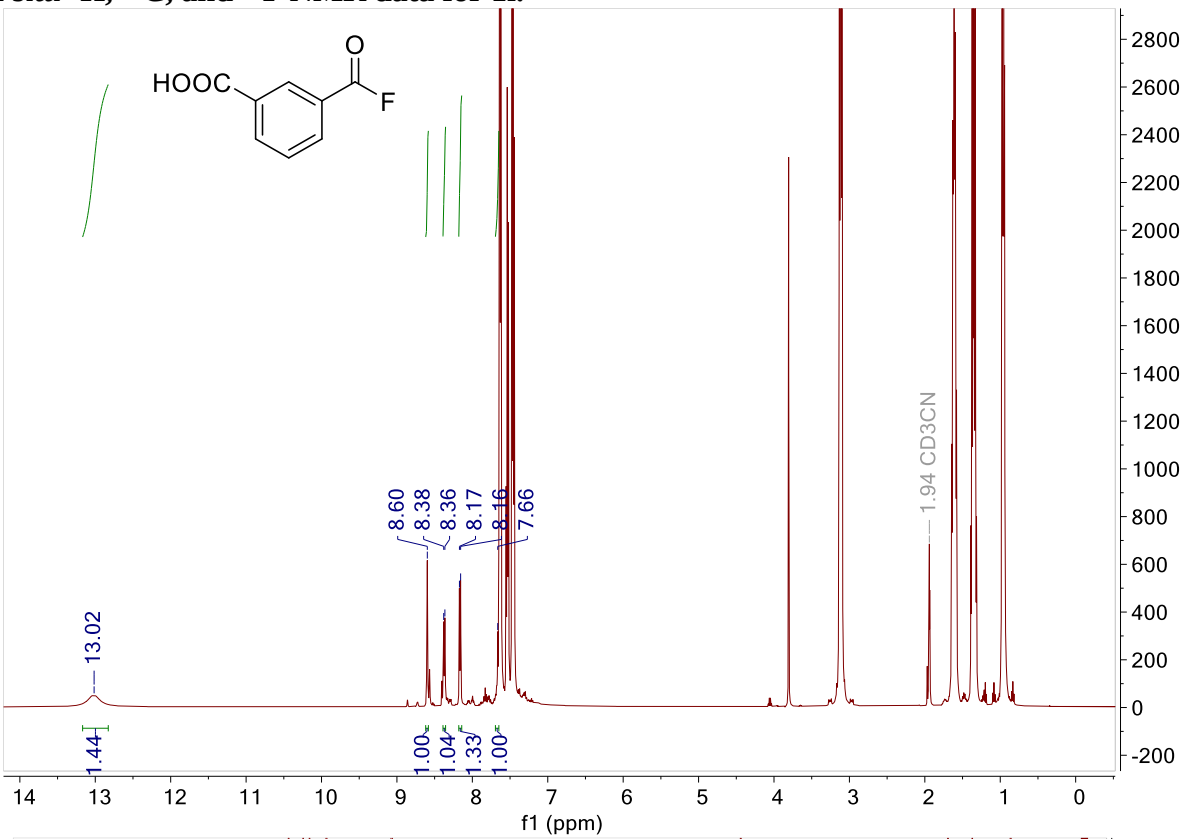
f1 (ppm)

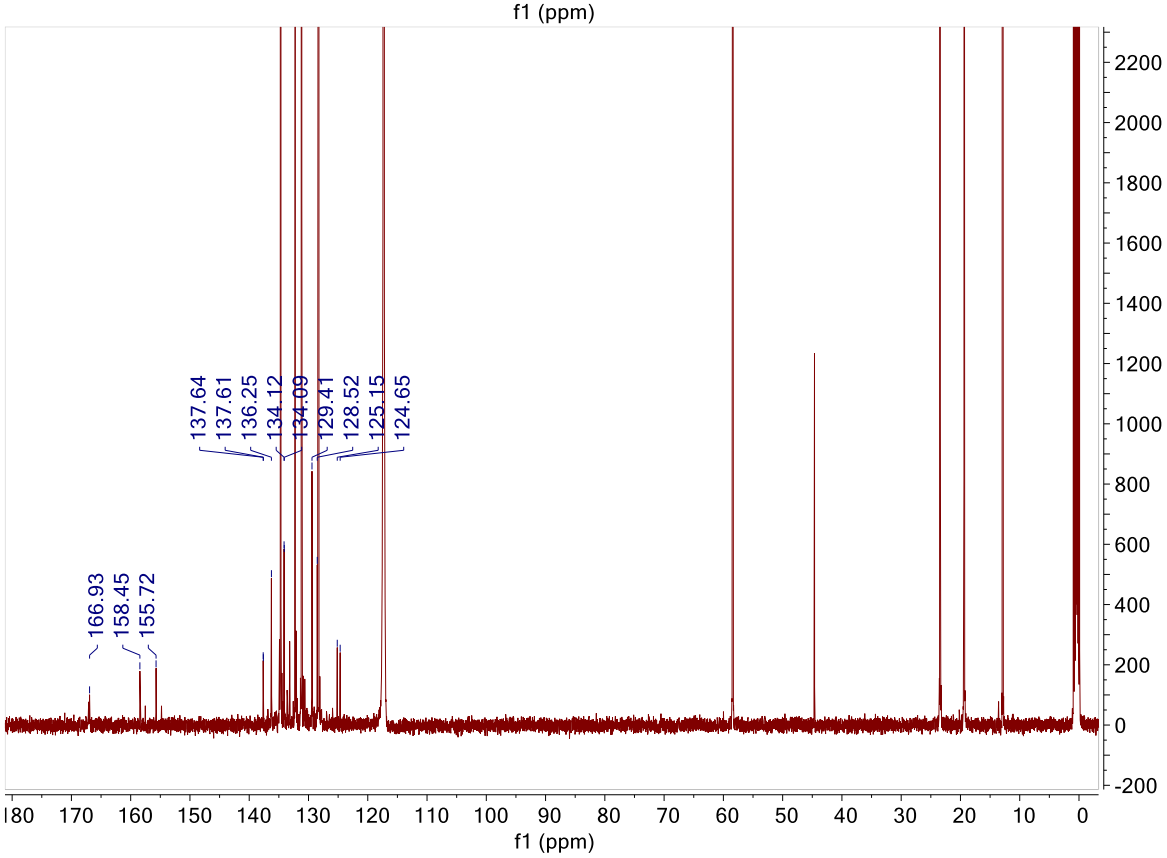
^{1}H and ^{13}C NMR data for 5h.

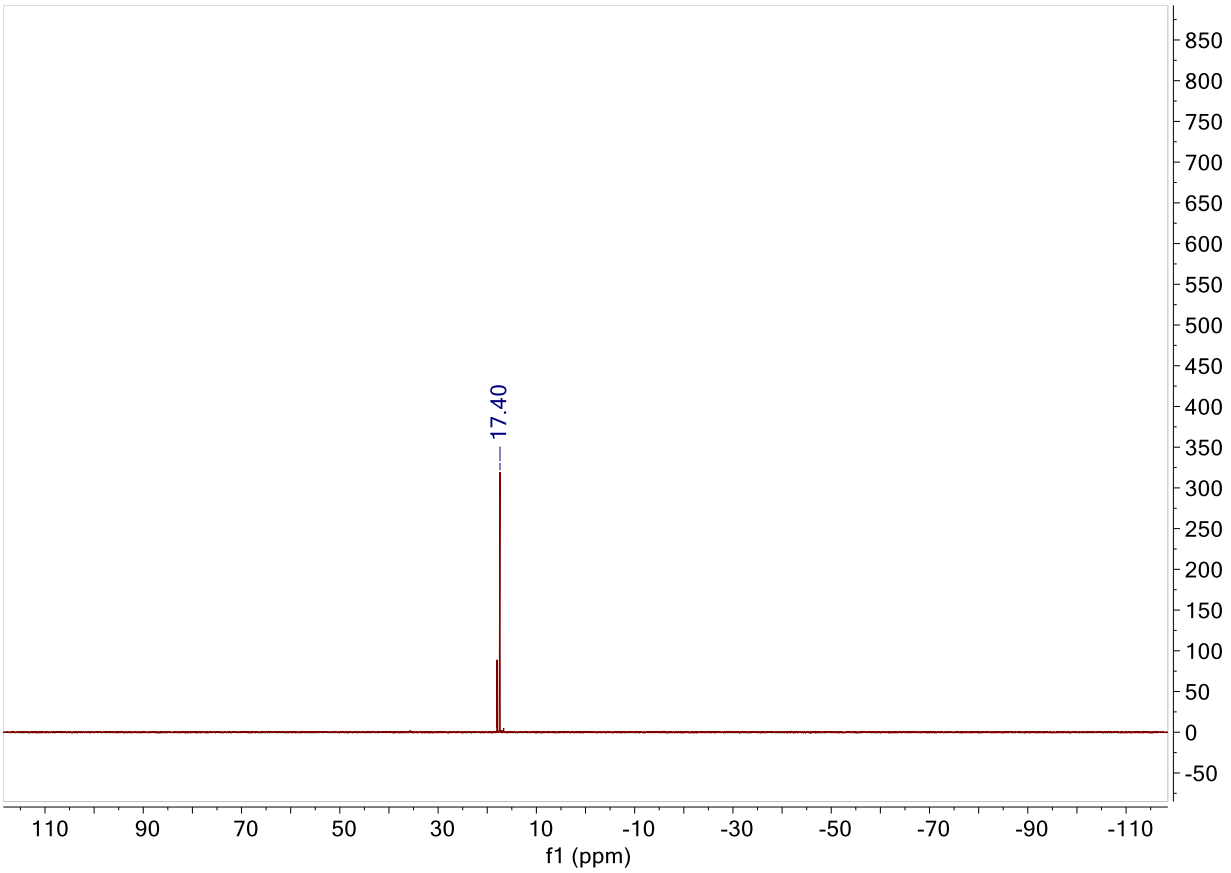




***In situ* ^{1}H, ^{13}C, and ^{19}F NMR data for 1i.**



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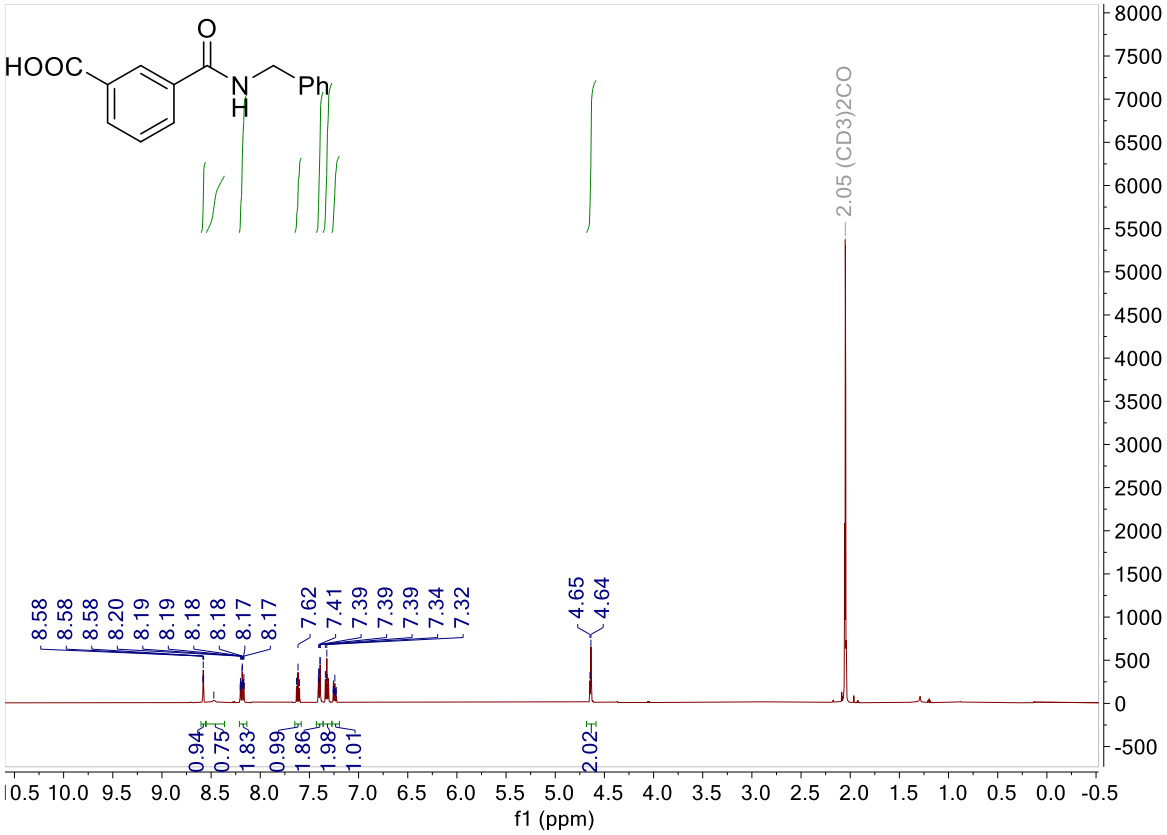
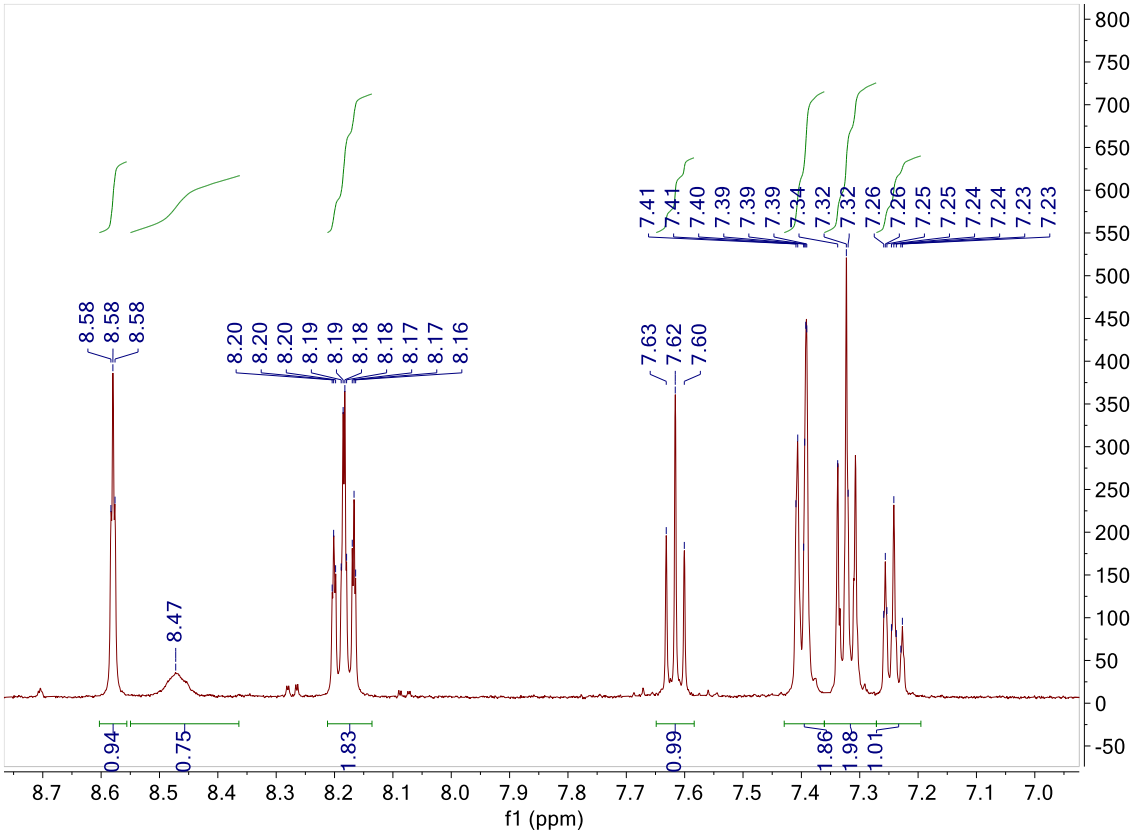
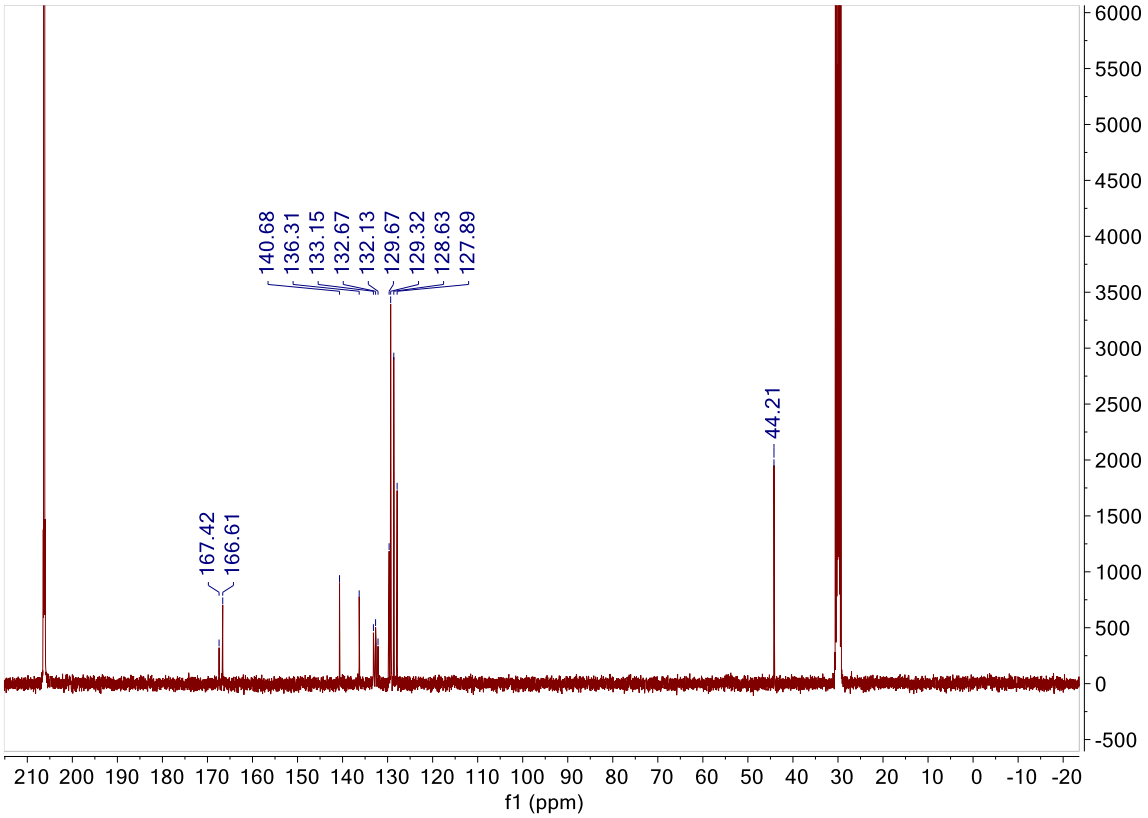
f1 (ppm)

^{1}H and ^{13}C NMR data for 5i.



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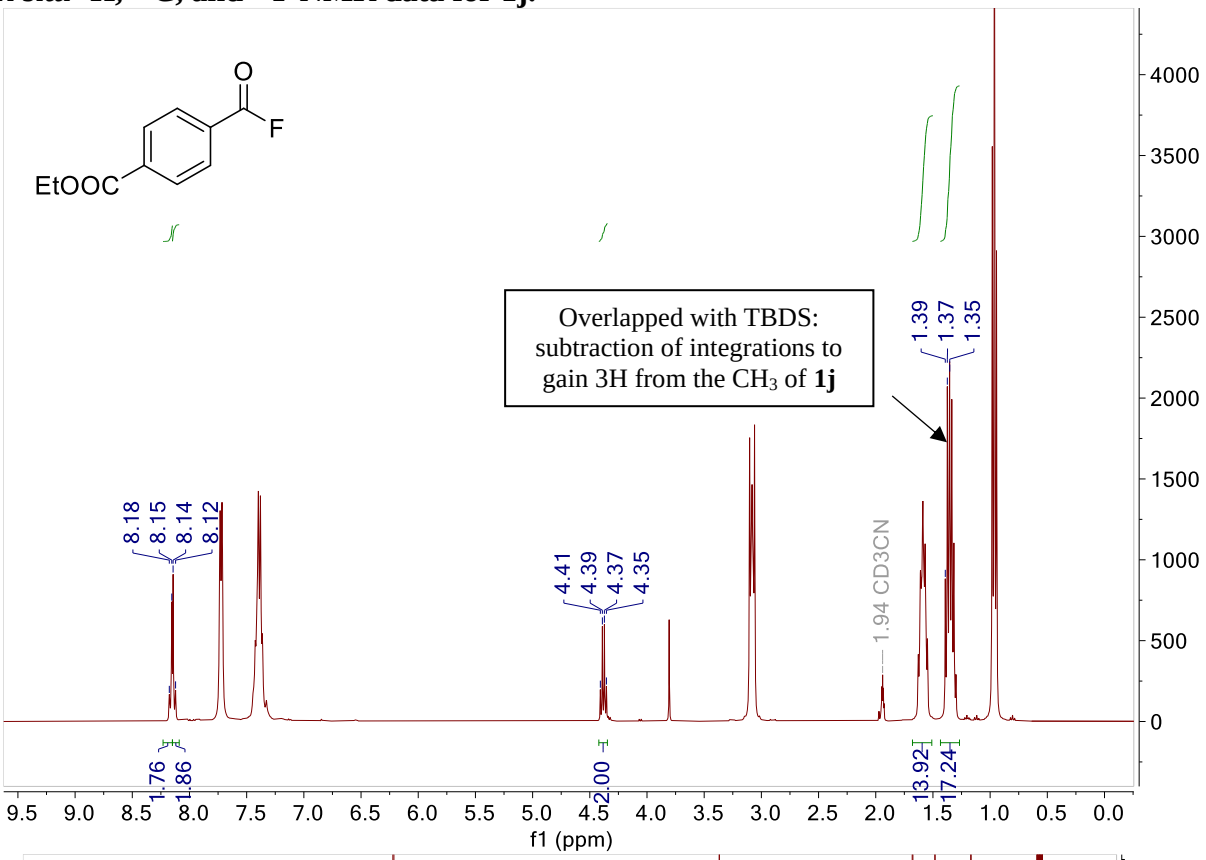
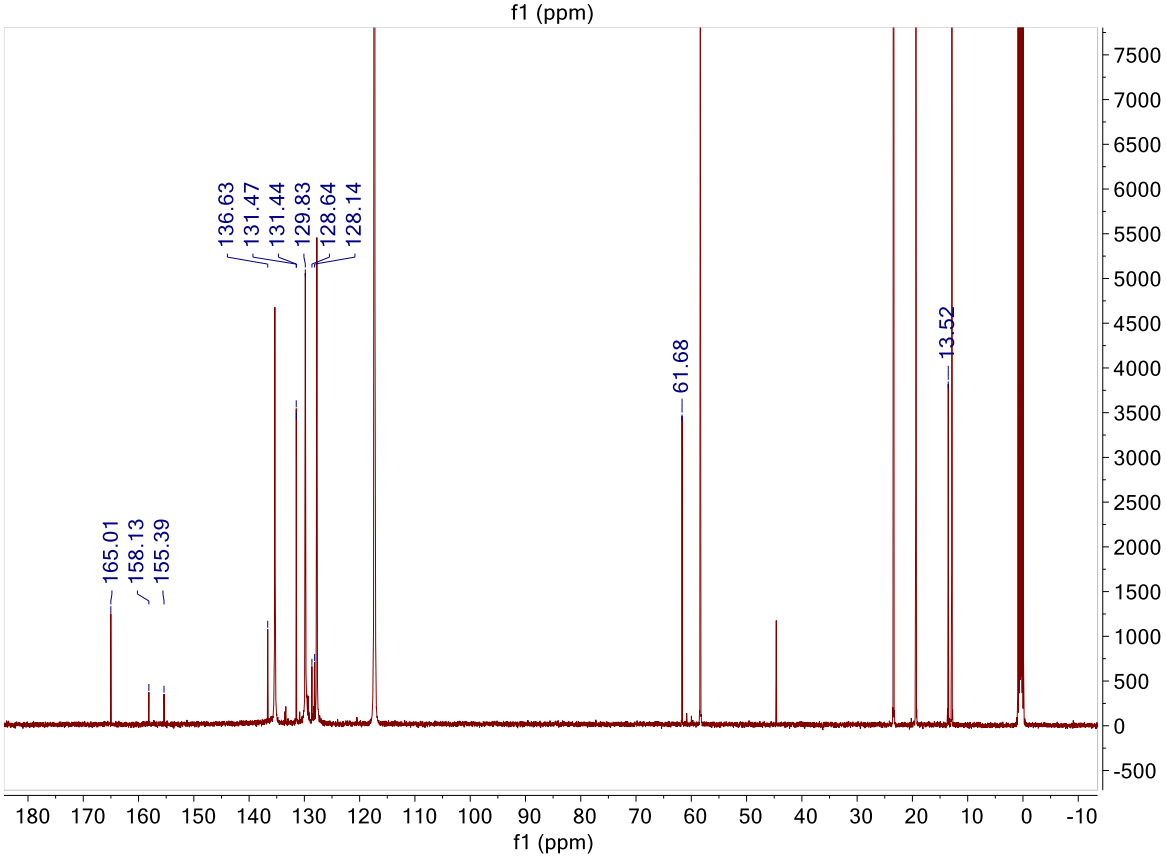
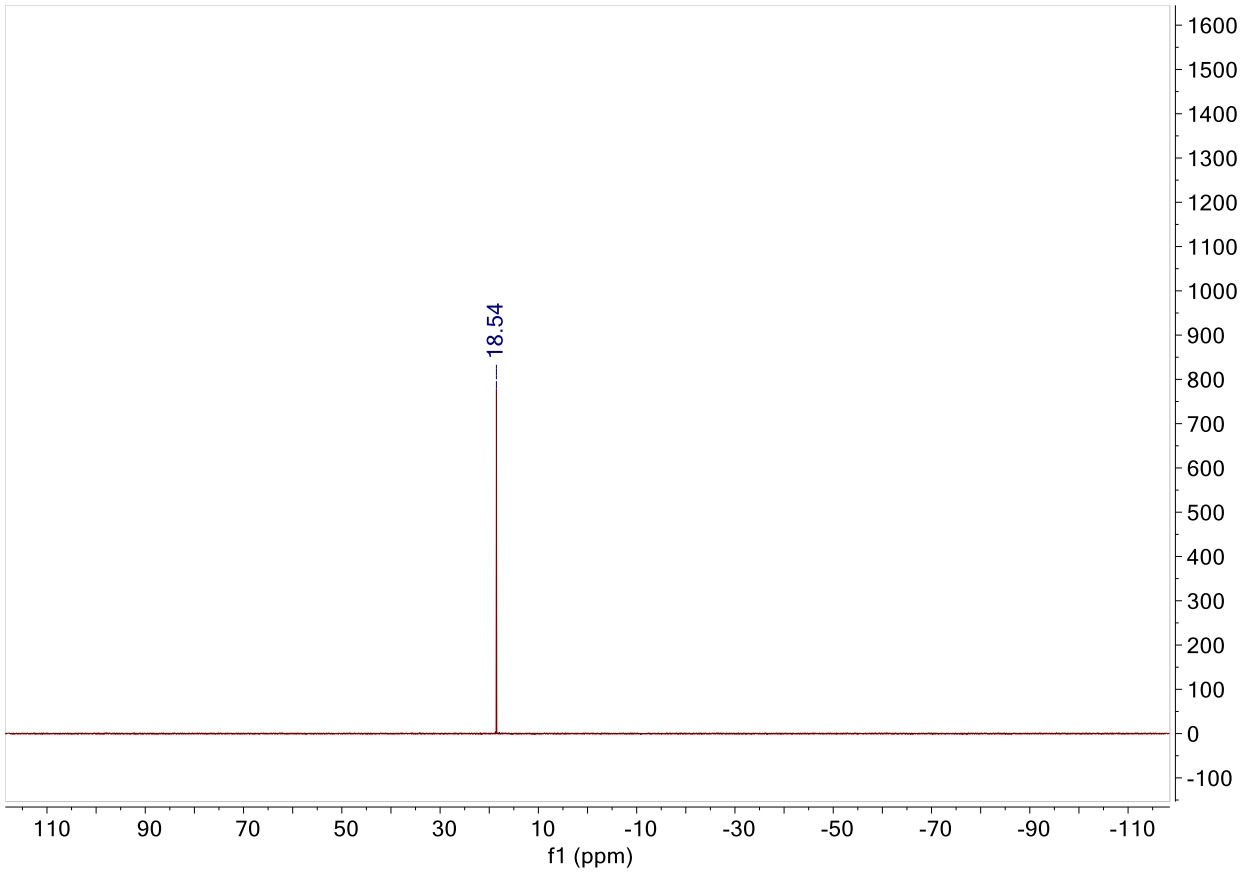
f1 (ppm)

***In situ* ^{1}H, ^{13}C, and ^{19}F NMR data for 1j.**



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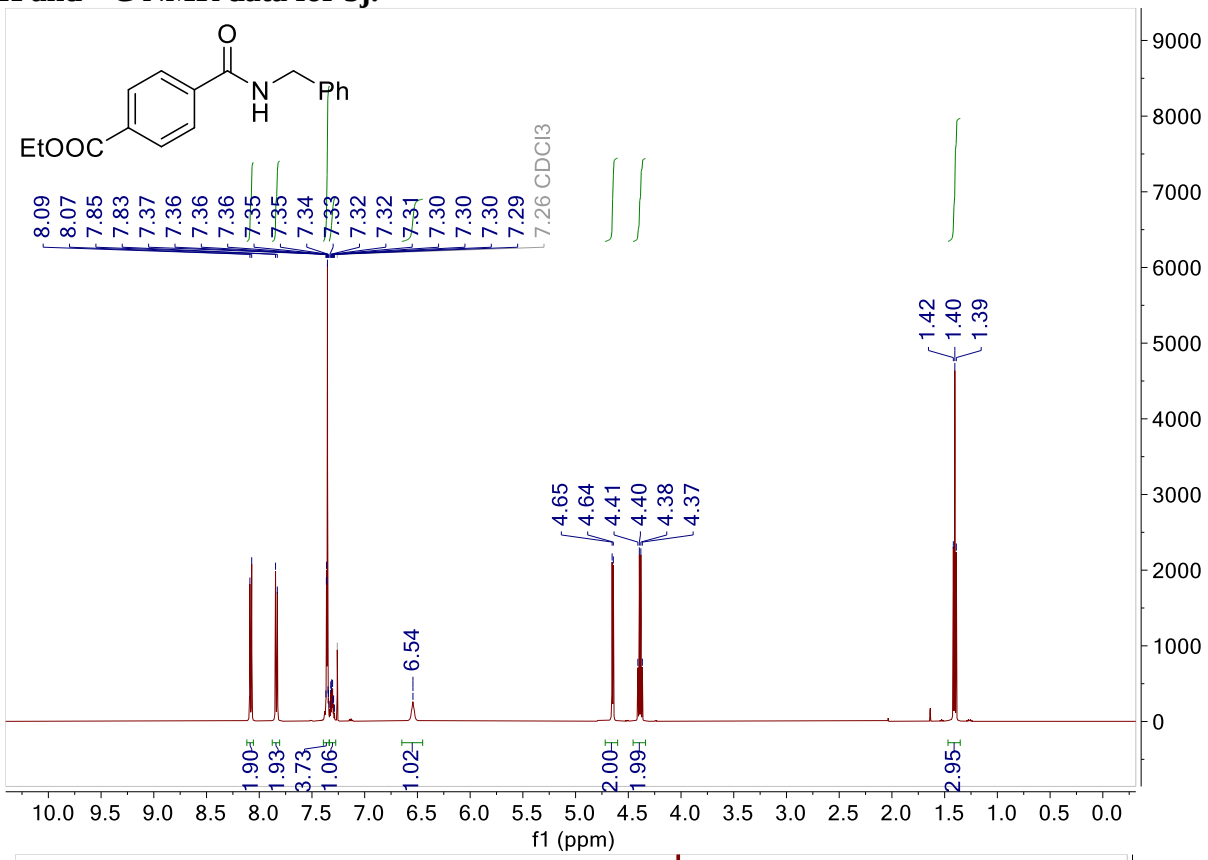
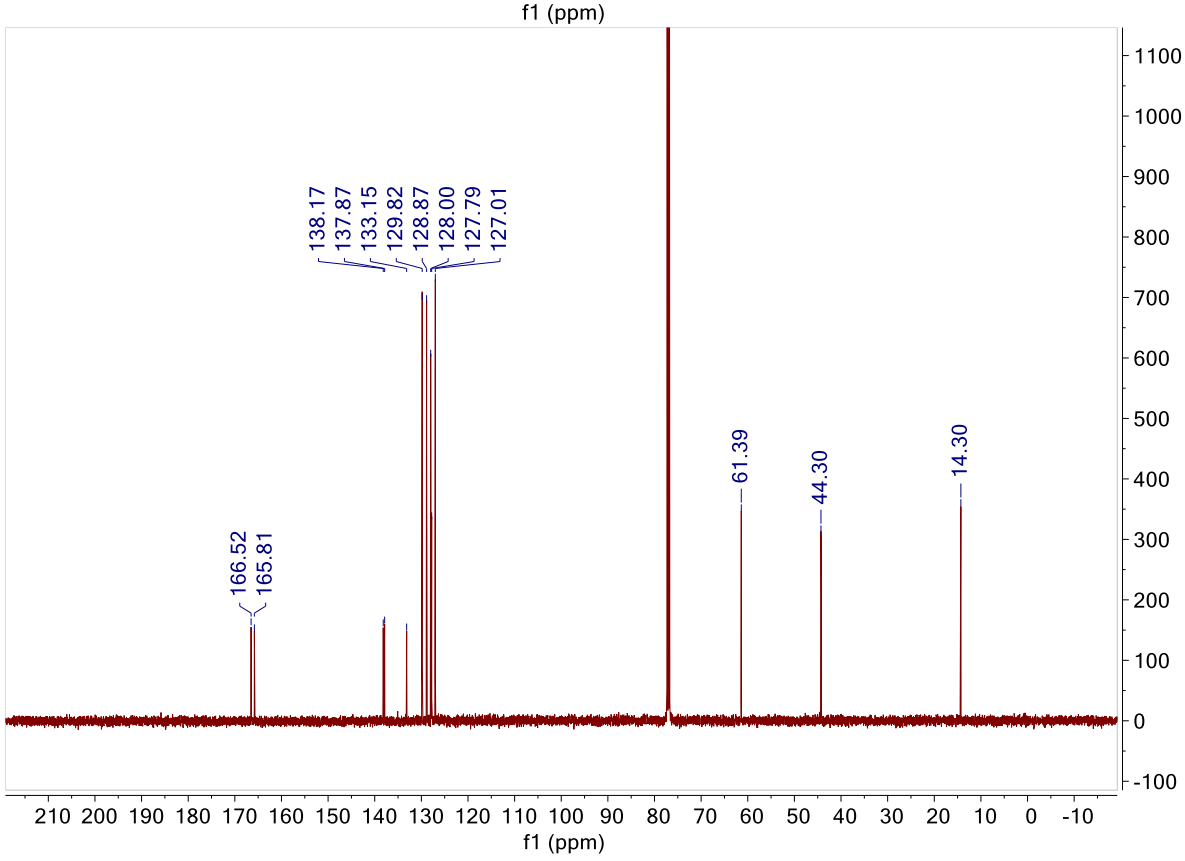
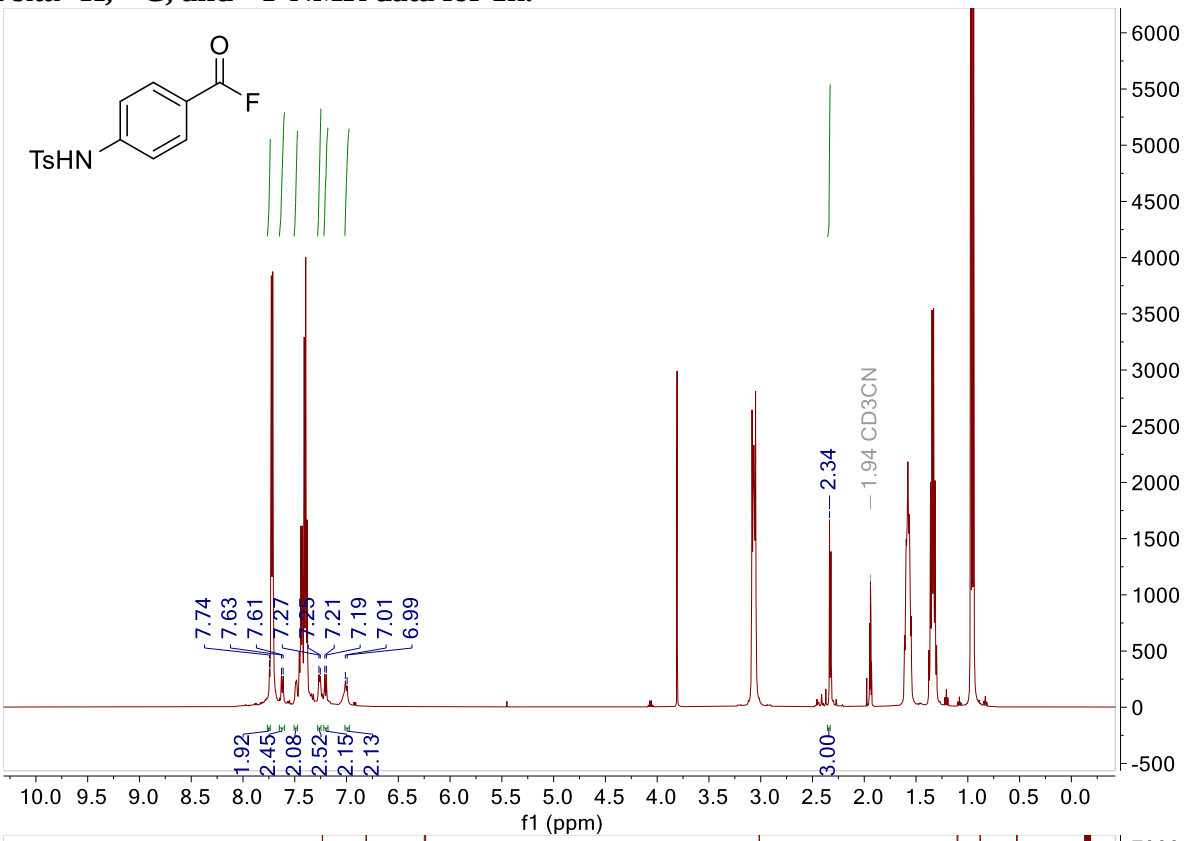
f1 (ppm)

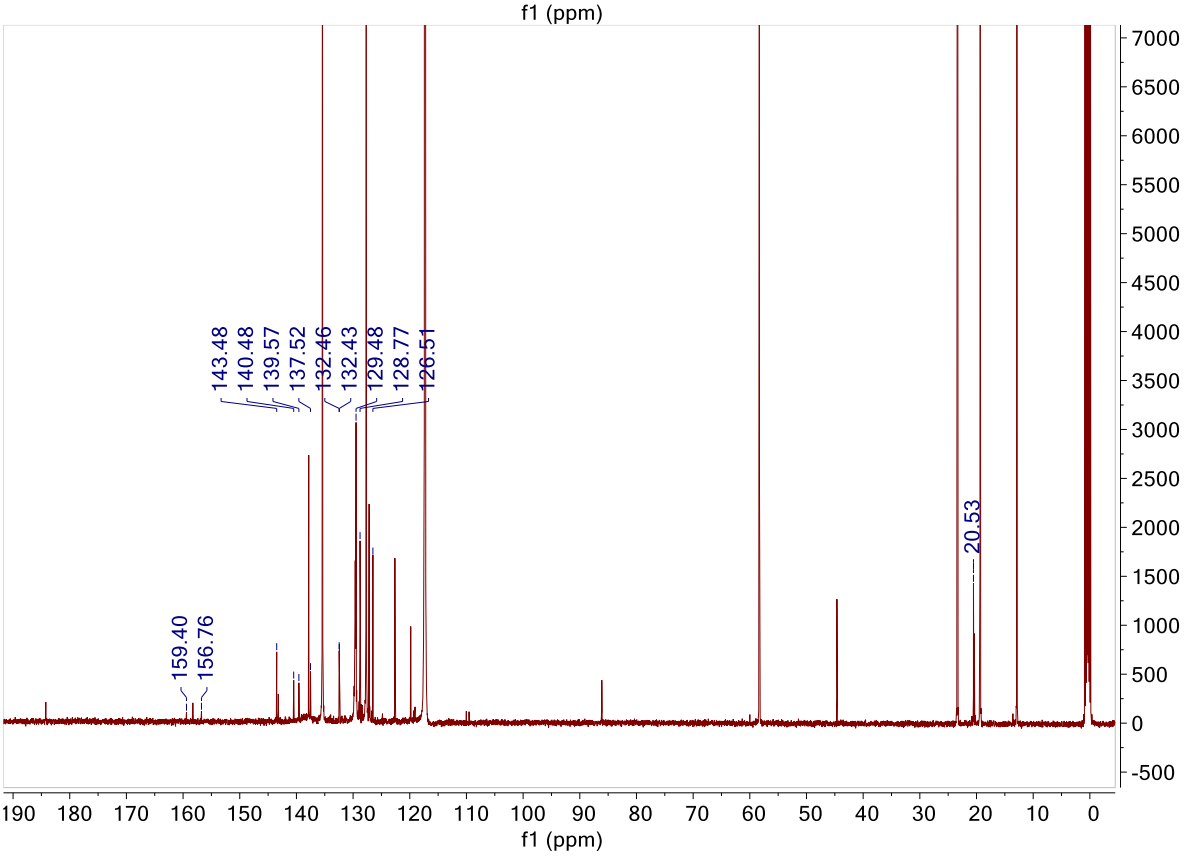
^{1}H and ^{13}C NMR data for 5j.

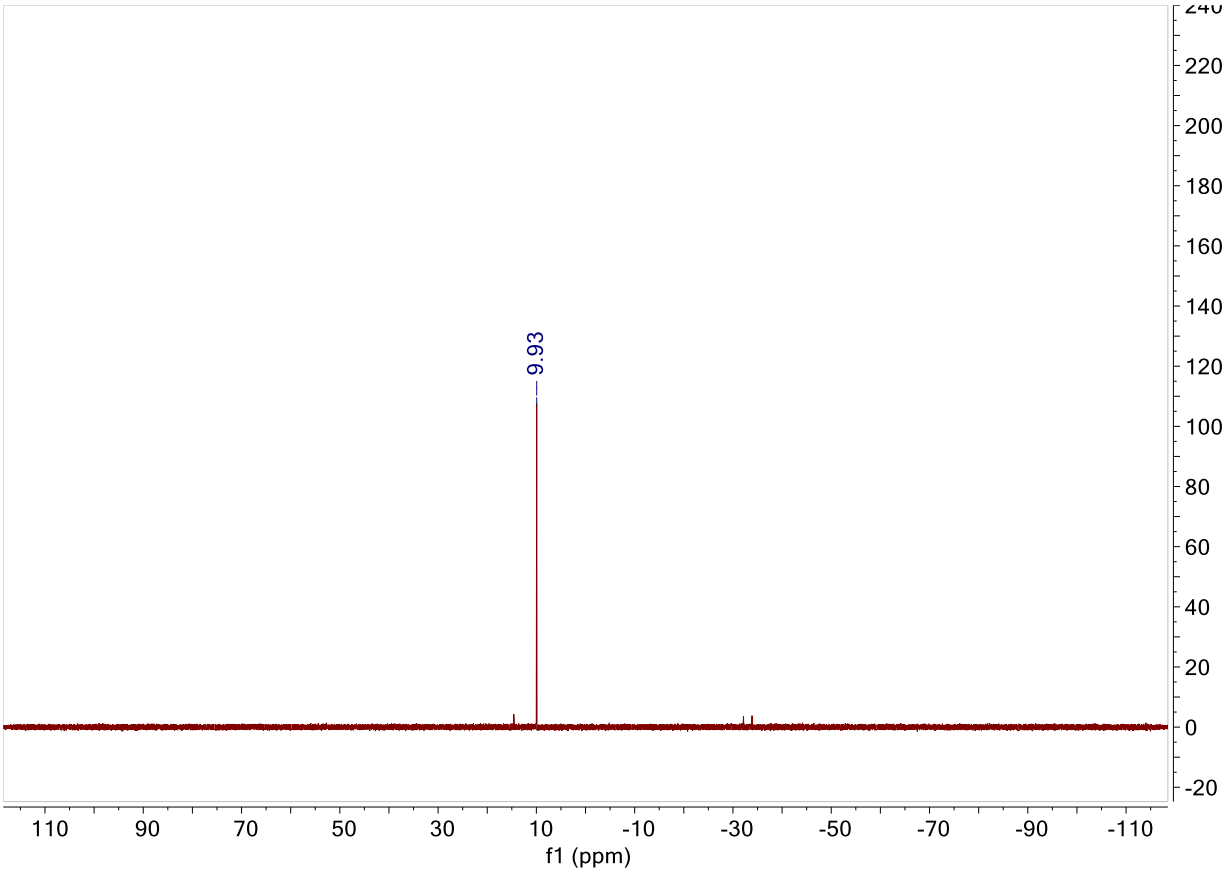




***In situ* ^{1}H, ^{13}C, and ^{19}F NMR data for 1k.**



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-70
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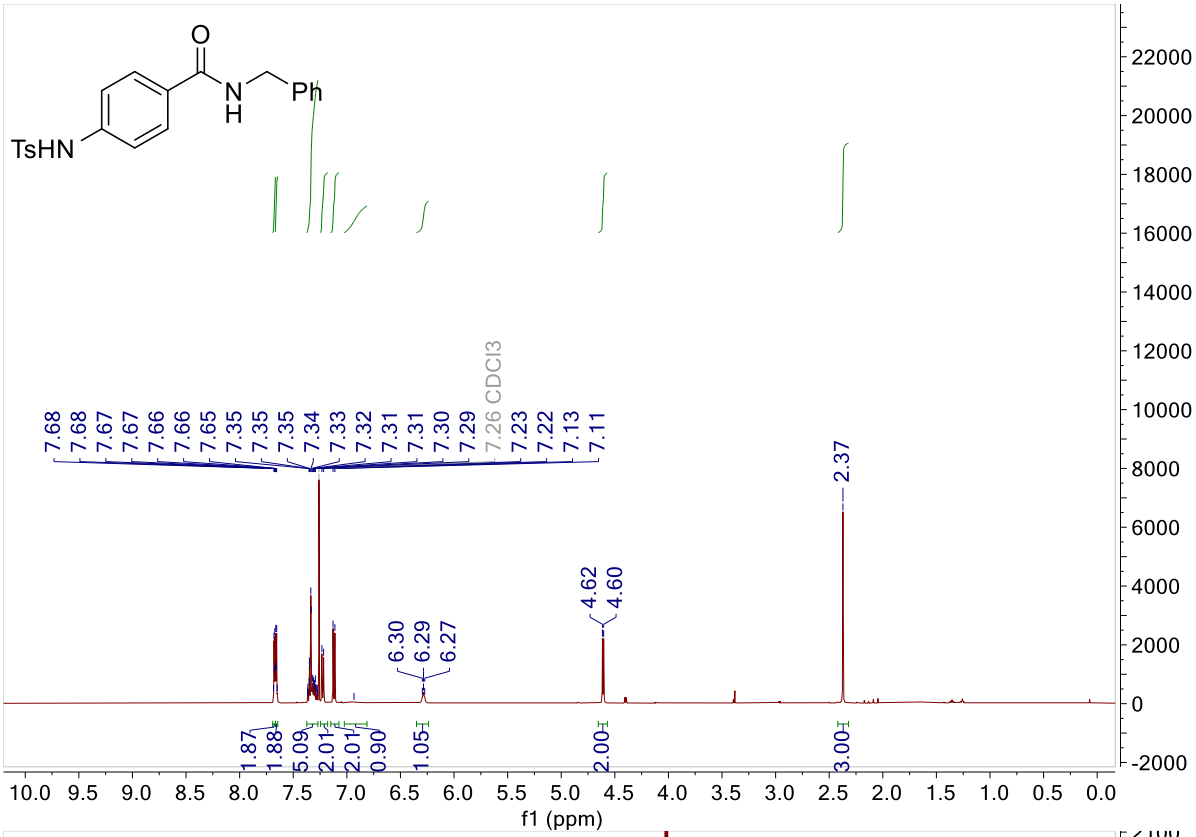
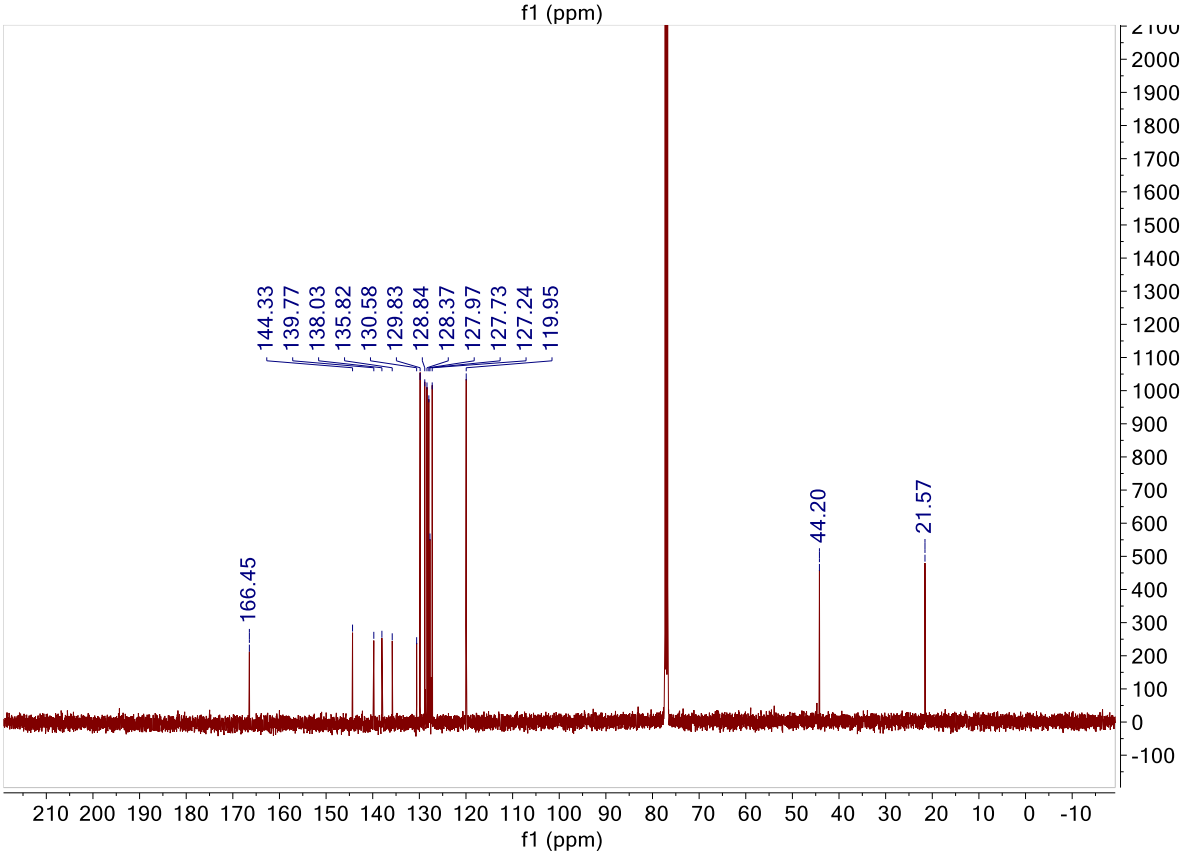
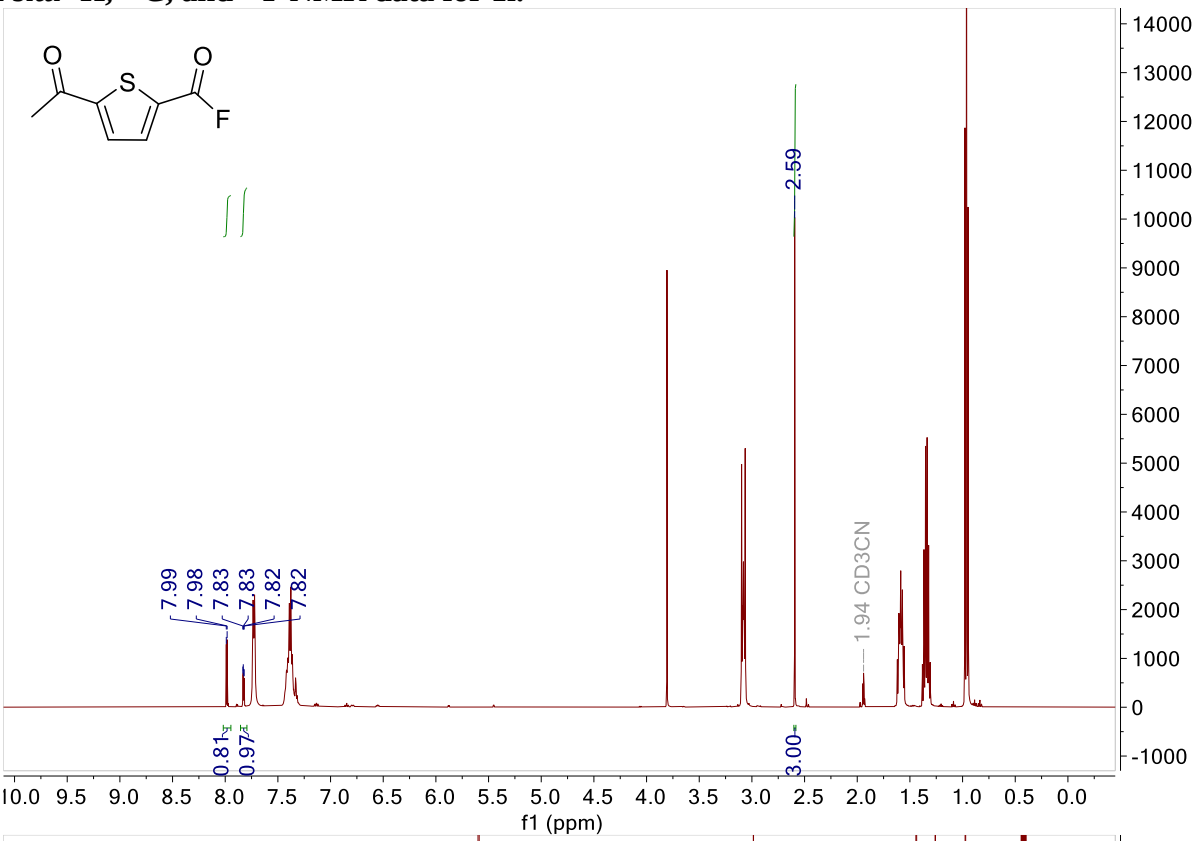
f1 (ppm)

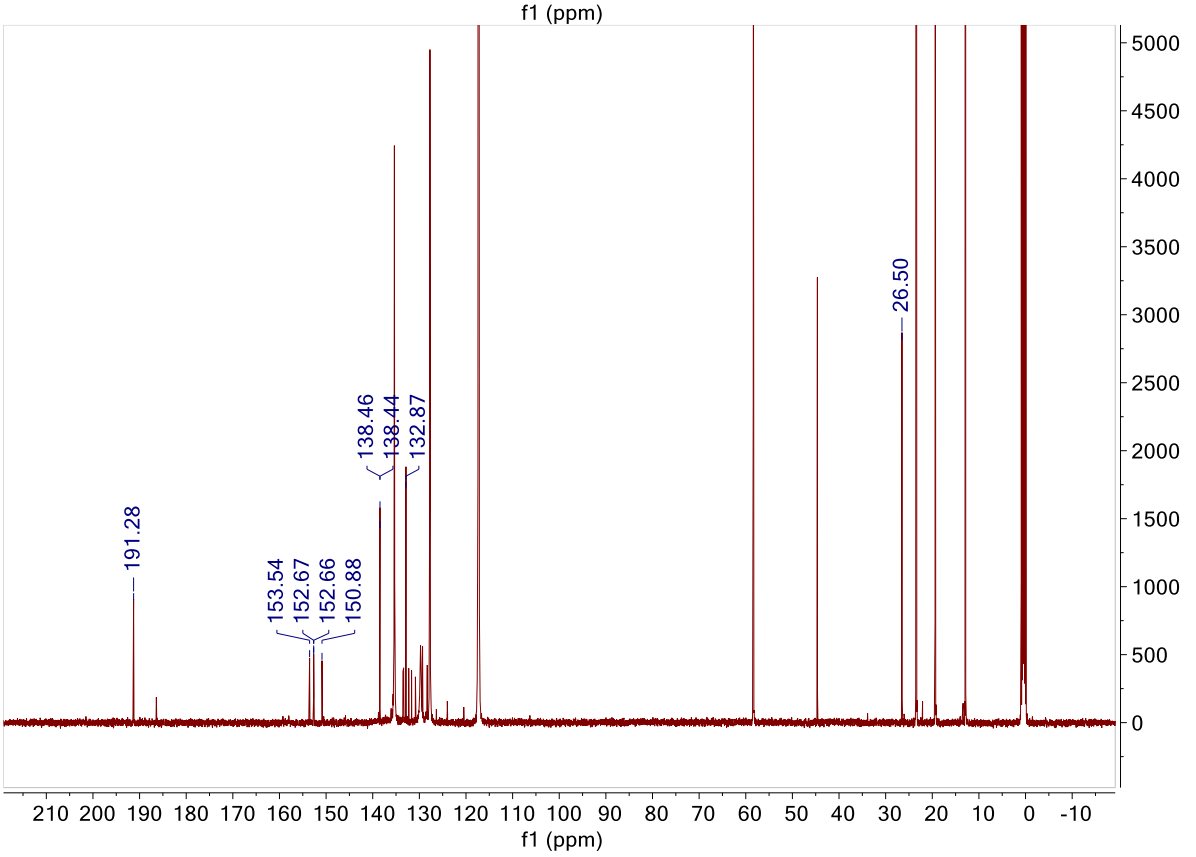
^{1}H and ^{13}C NMR data for 5k.

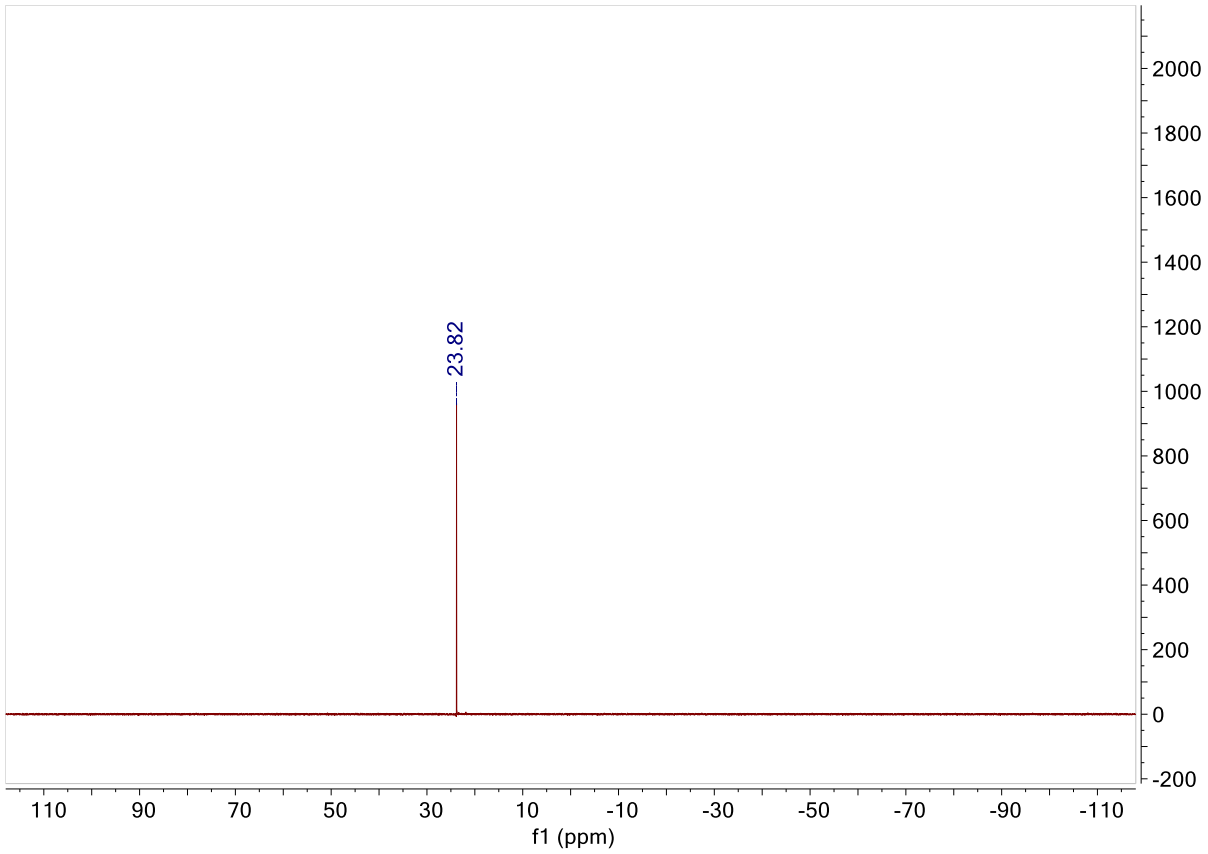




***In situ* ^{1}H, ^{13}C, and ^{19}F NMR data for 1l.**



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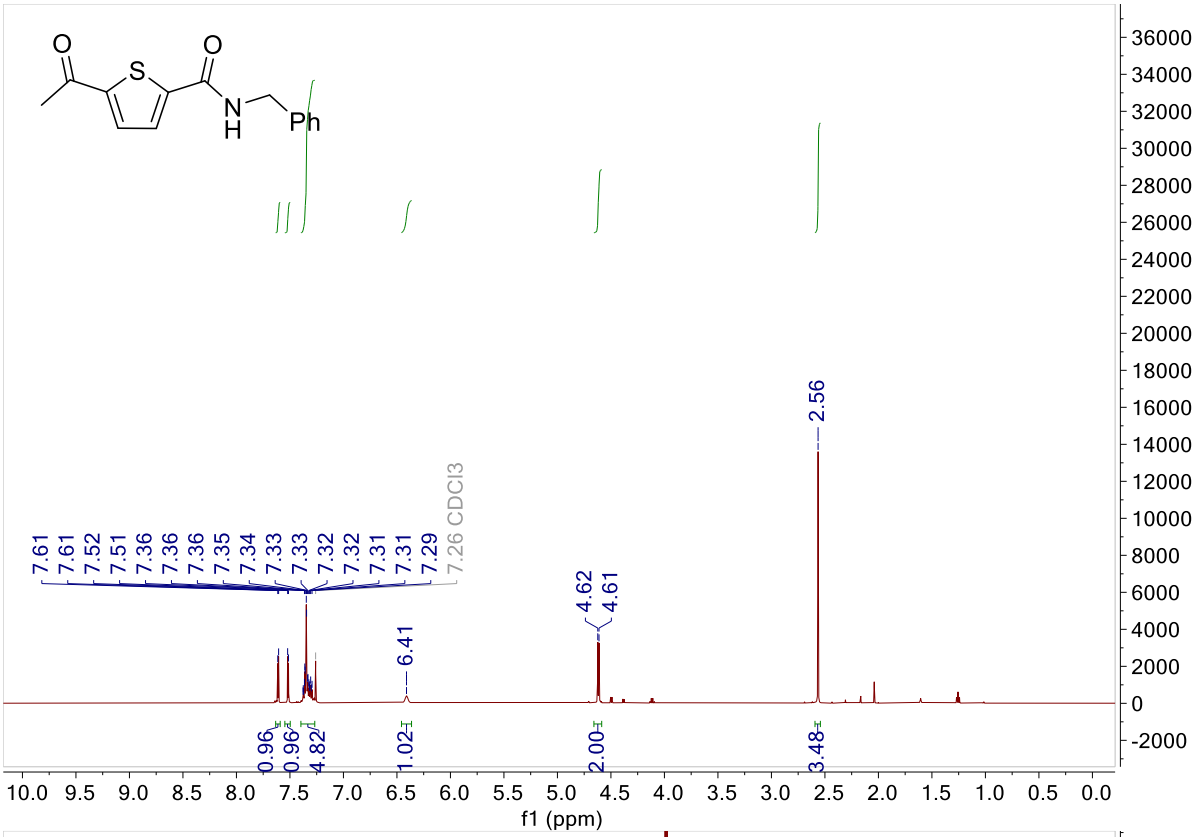
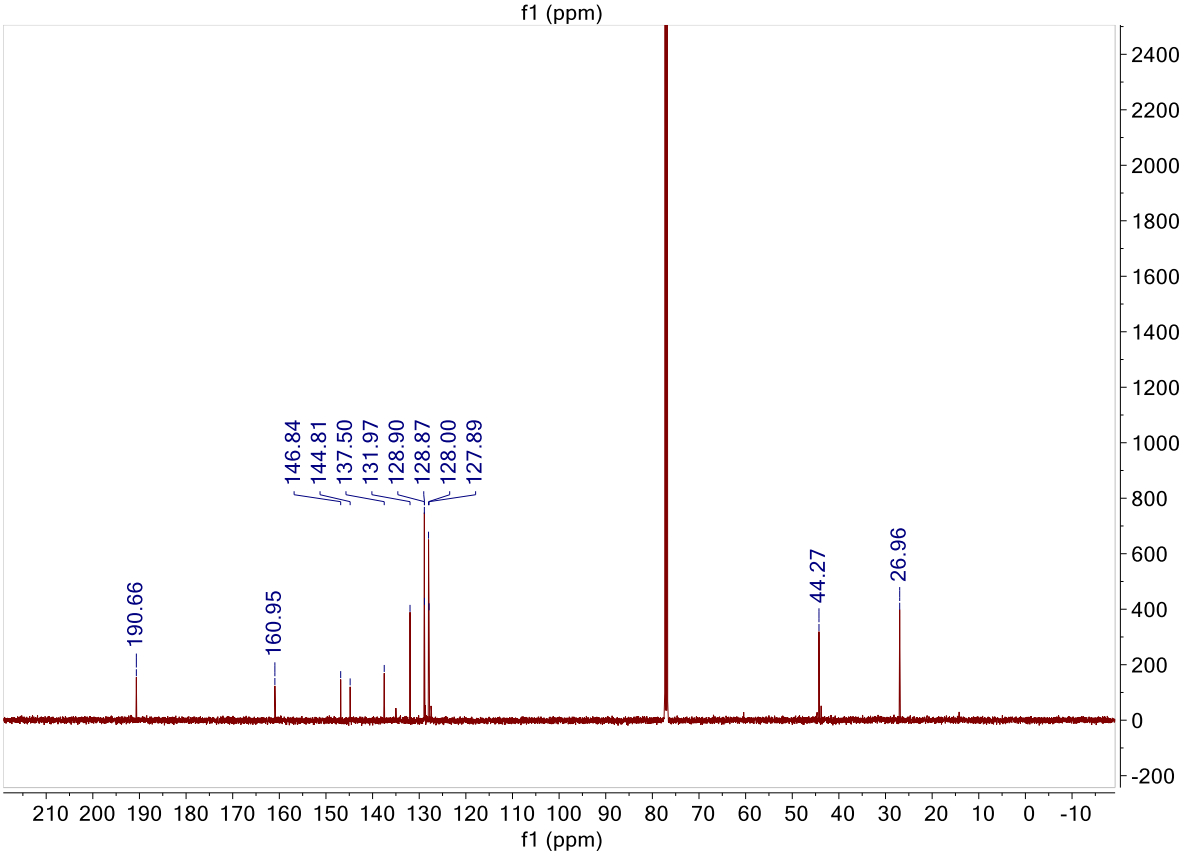
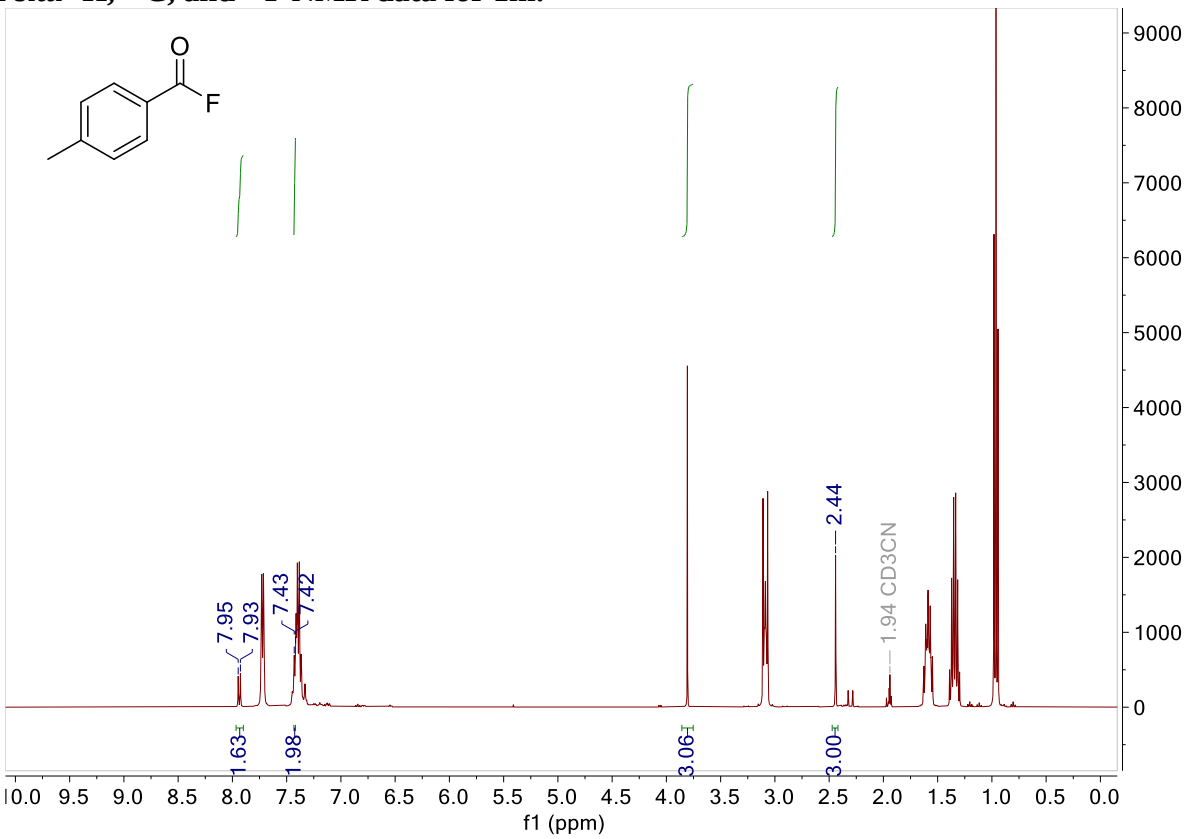
f1 (ppm)

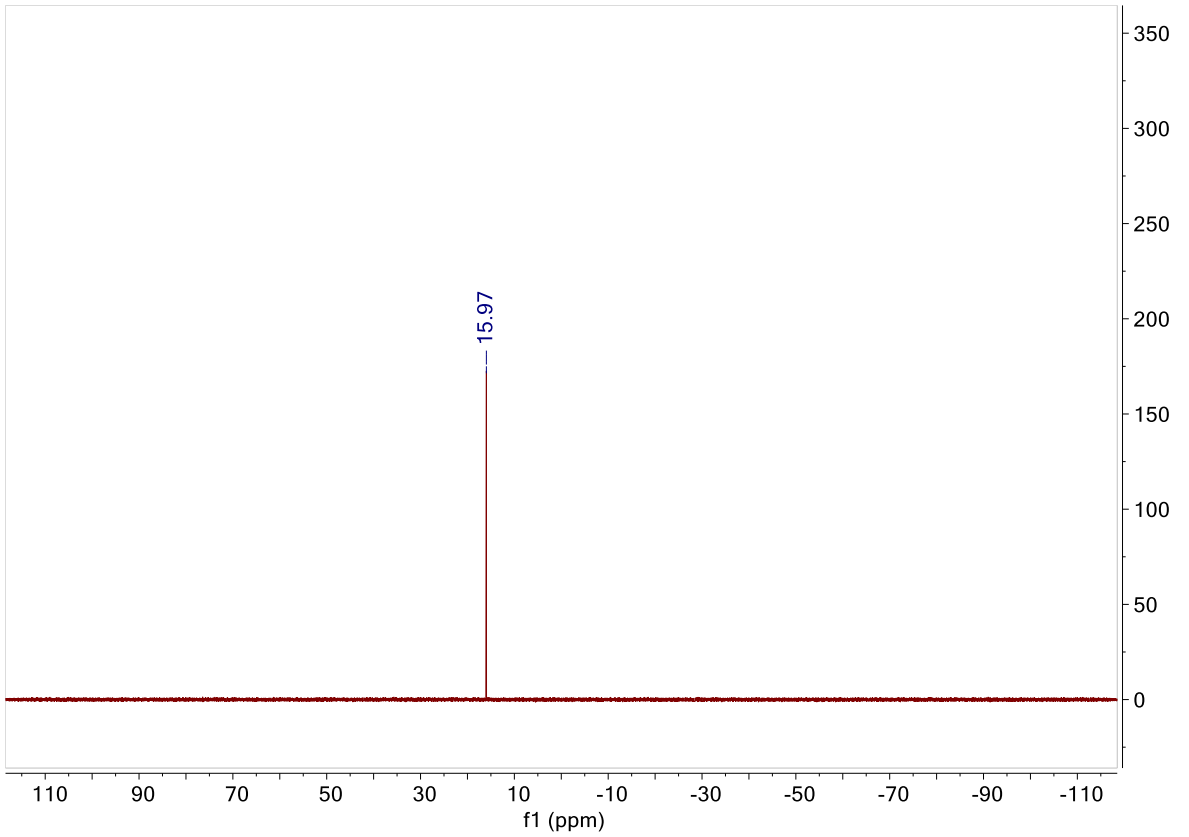
^{1}H and ^{13}C NMR data for 5l.



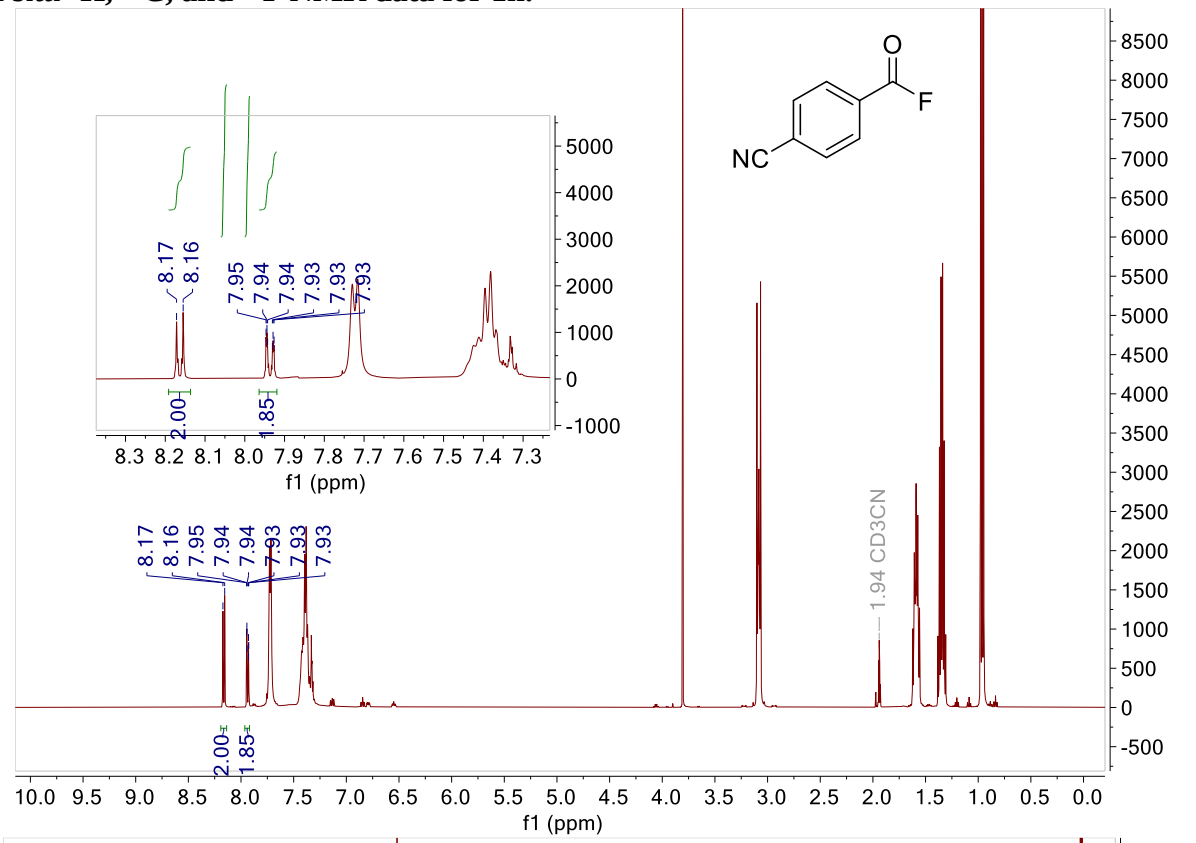


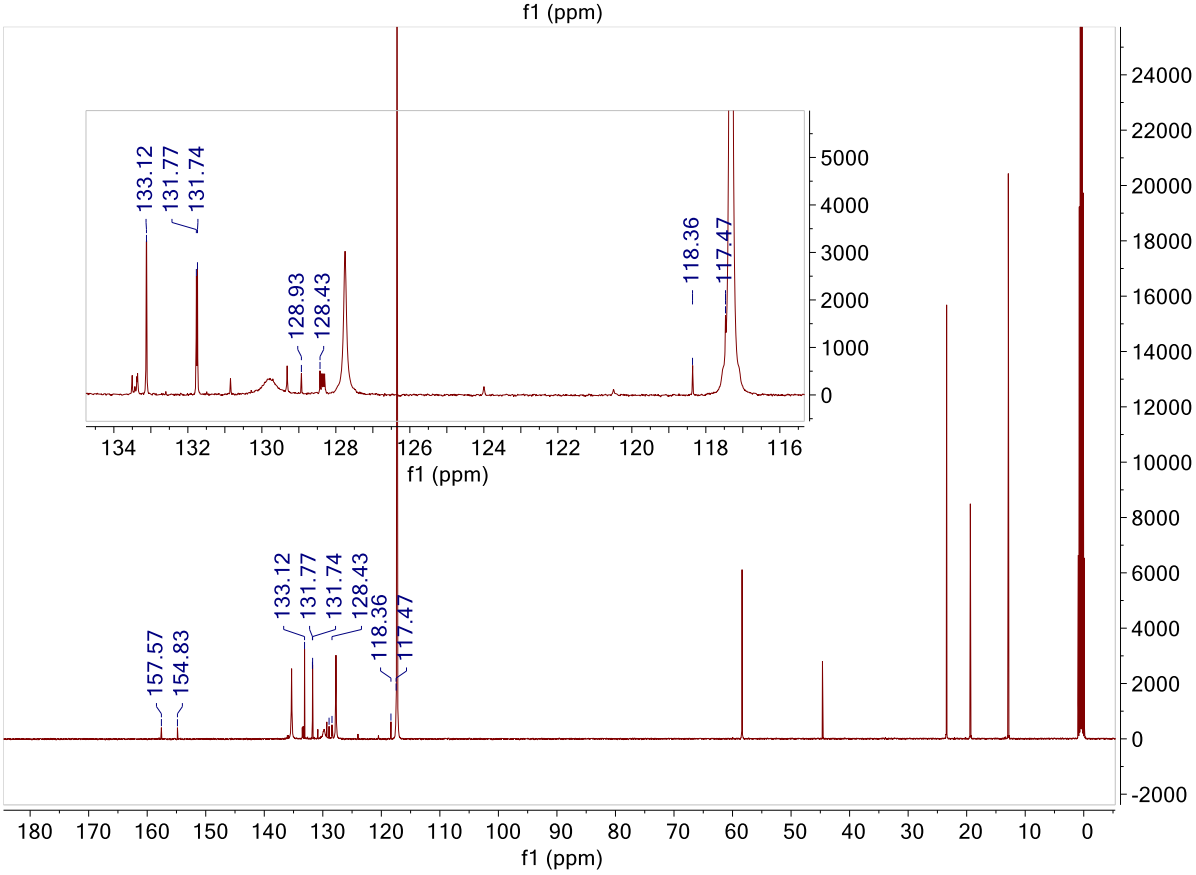
***In situ* ^{1}H, ^{13}C, and ^{19}F NMR data for 1m.**

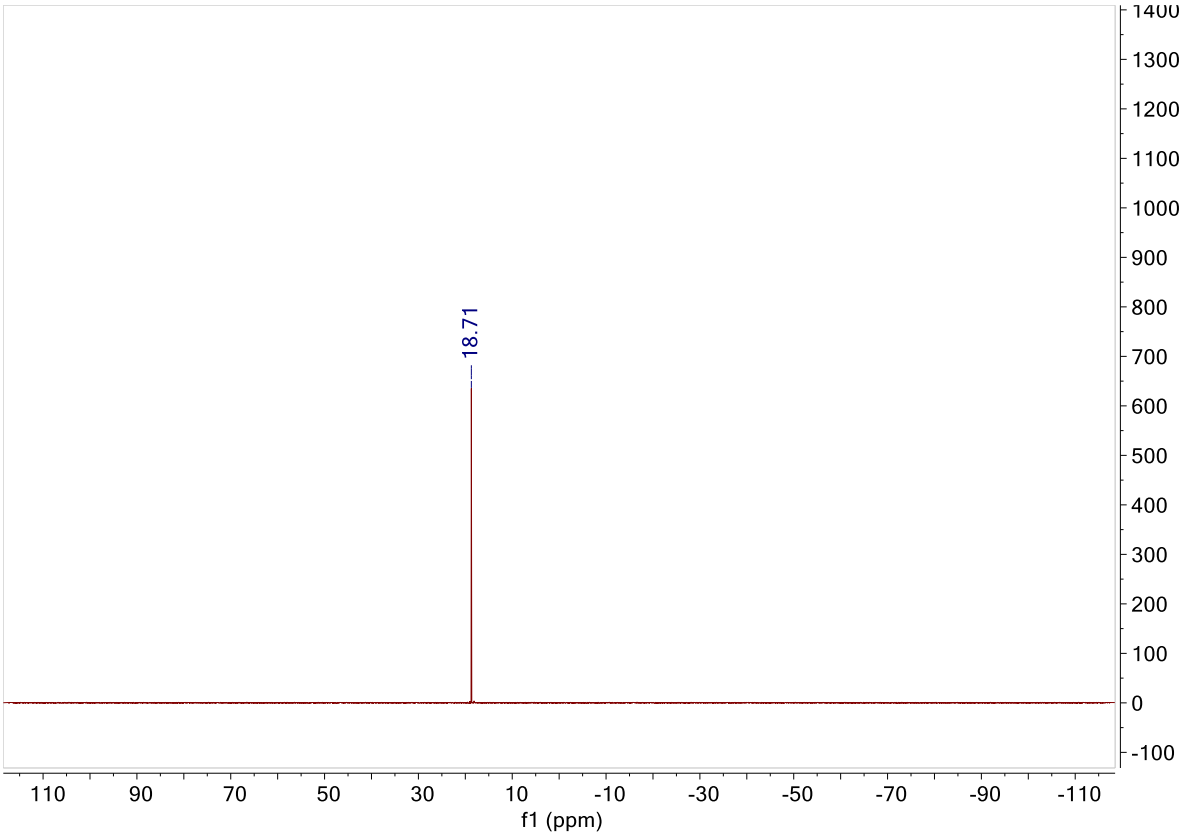




***In situ* ^{1}H, ^{13}C, and ^{19}F NMR data for 1n.**



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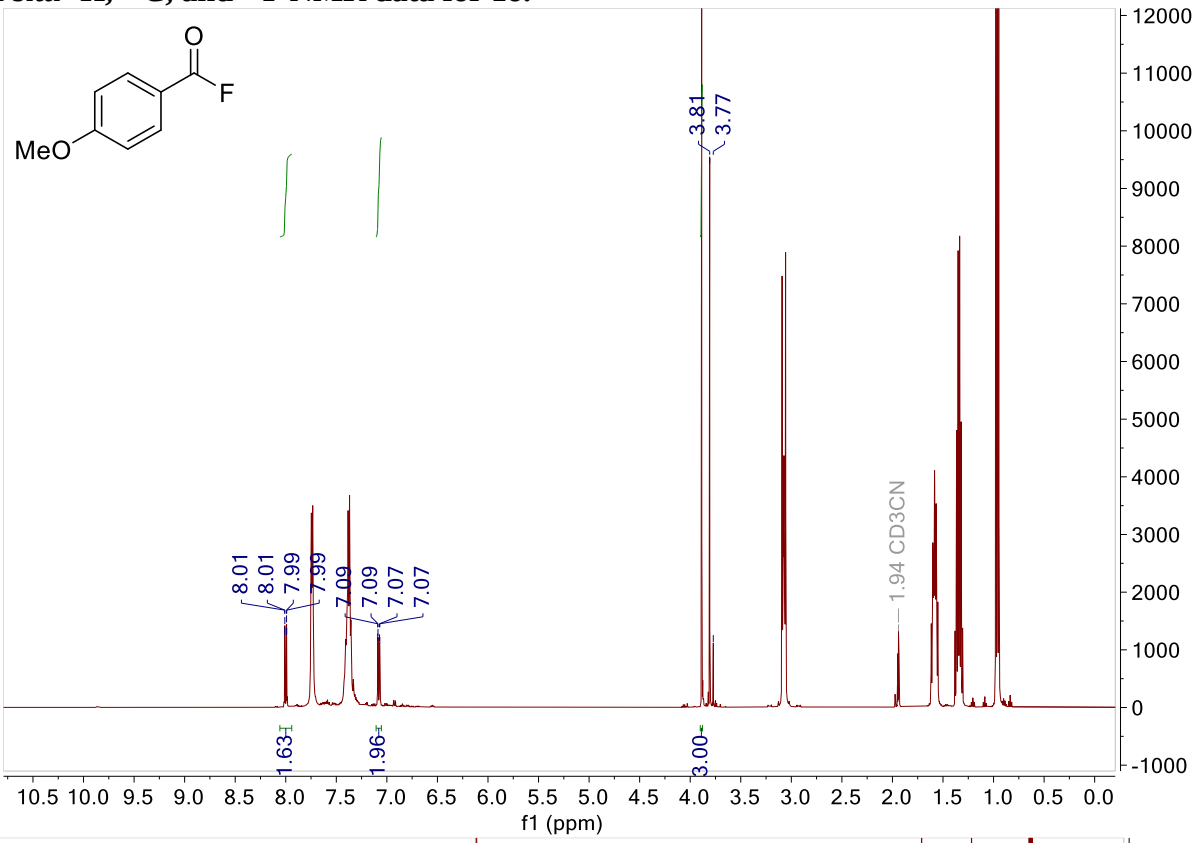
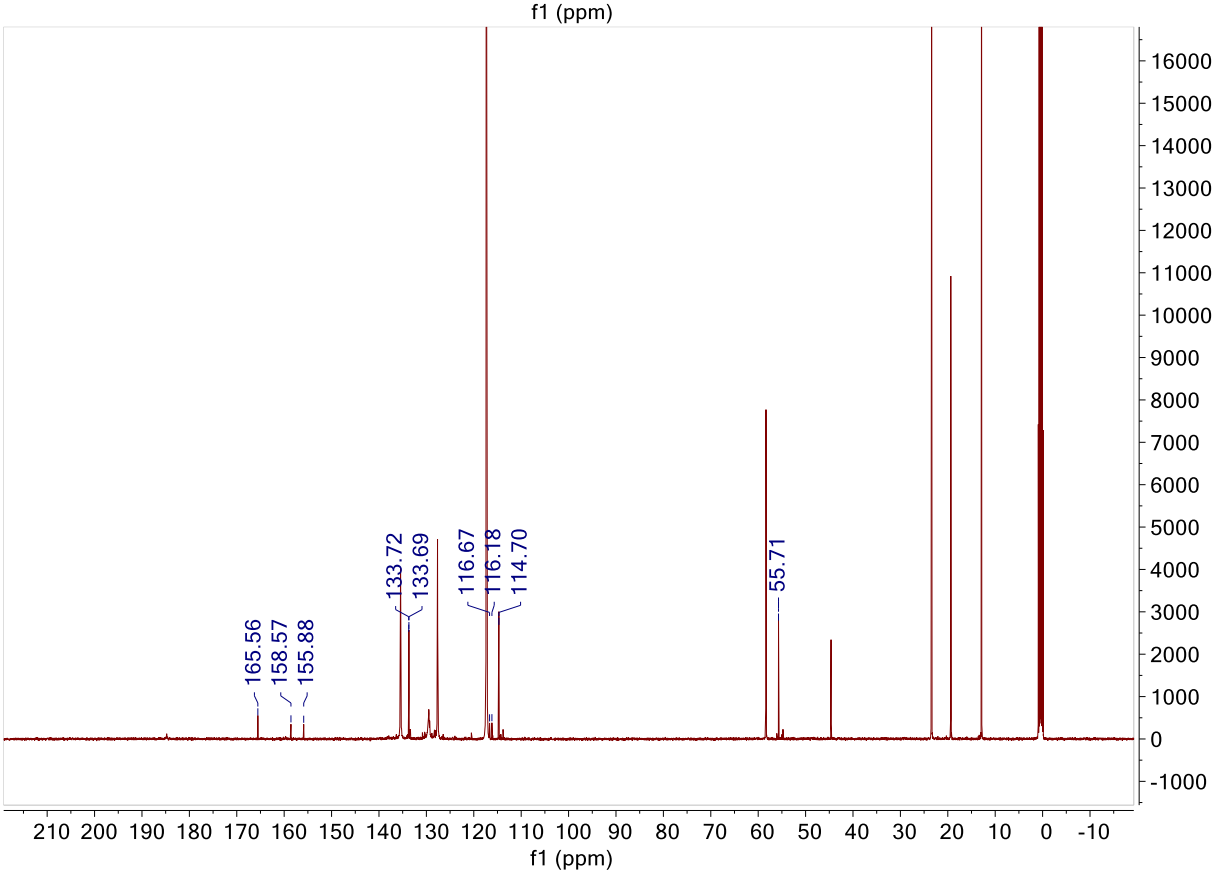
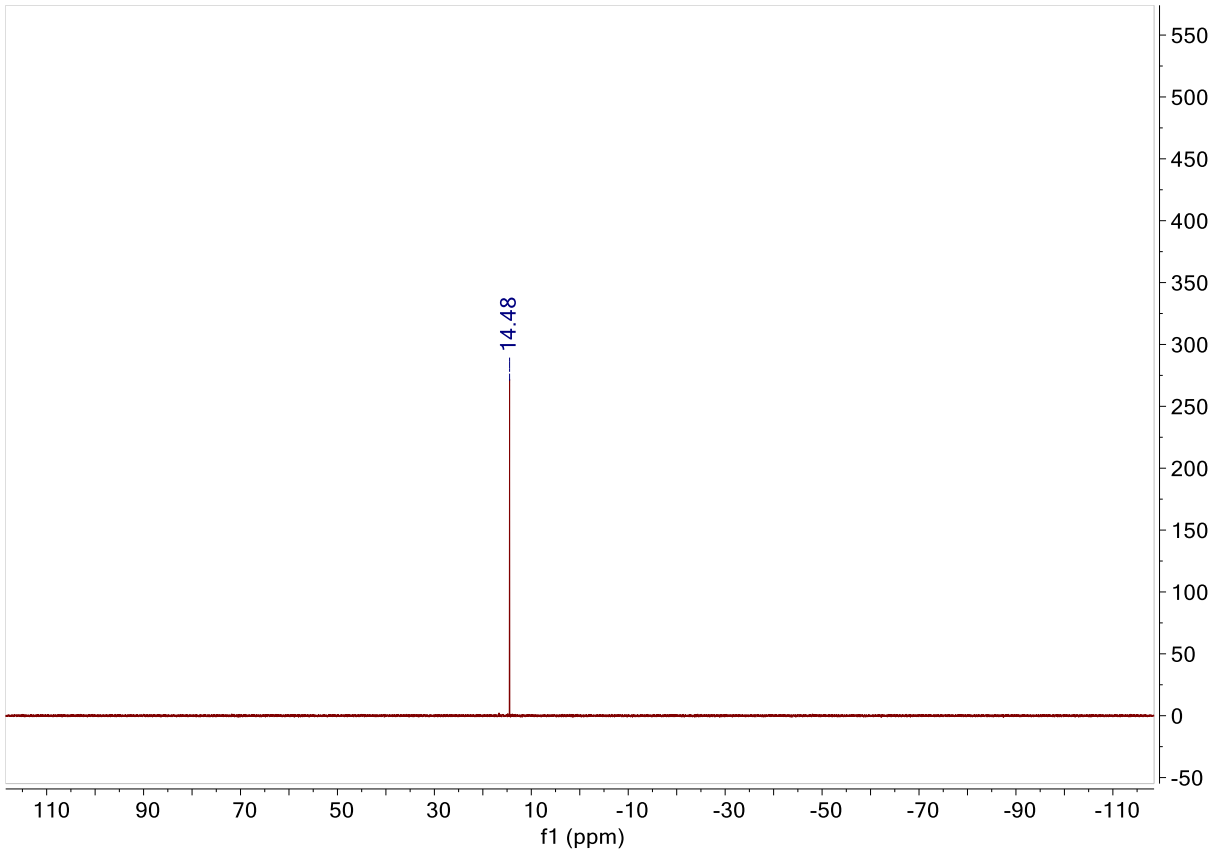
10
-10
-30
-50
-70
-90
-110
f1 (ppm)

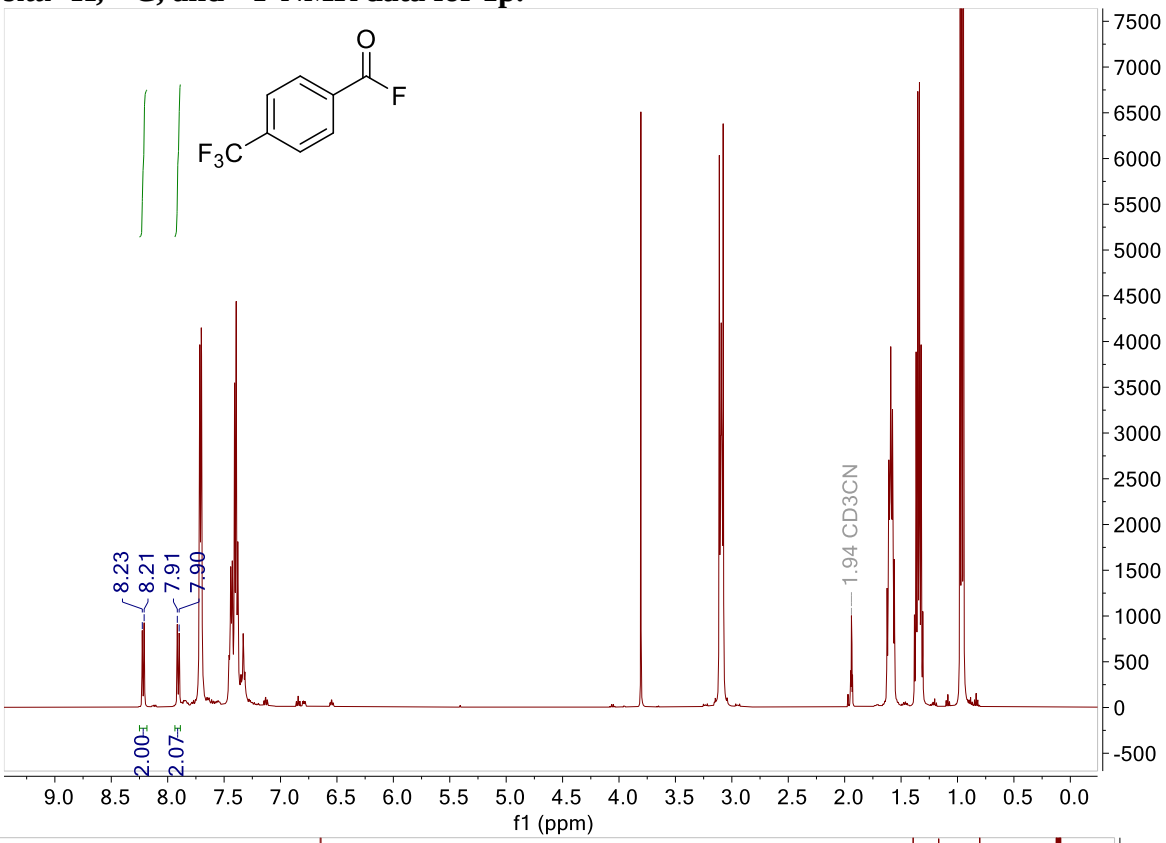
***In situ* ^{1}H, ^{13}C, and ^{19}F NMR data for 1o.**

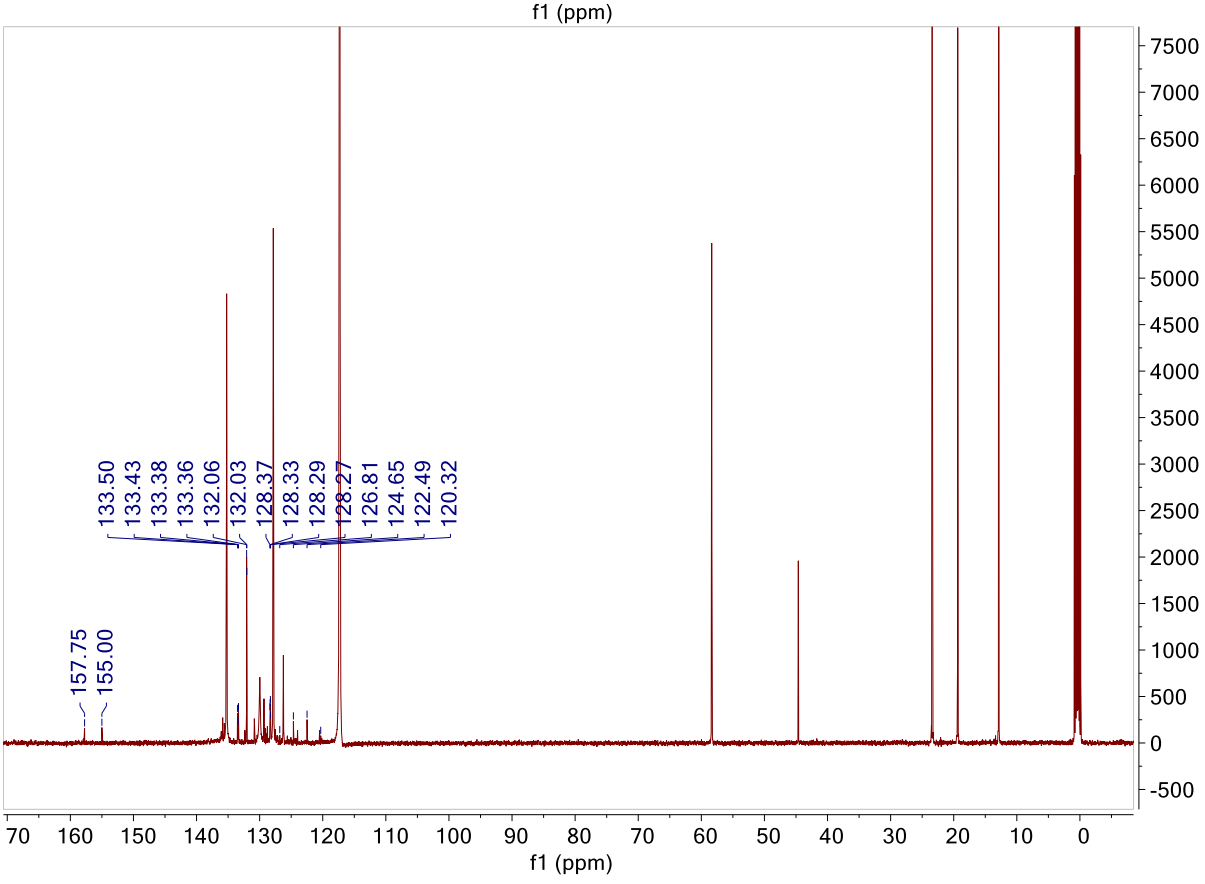


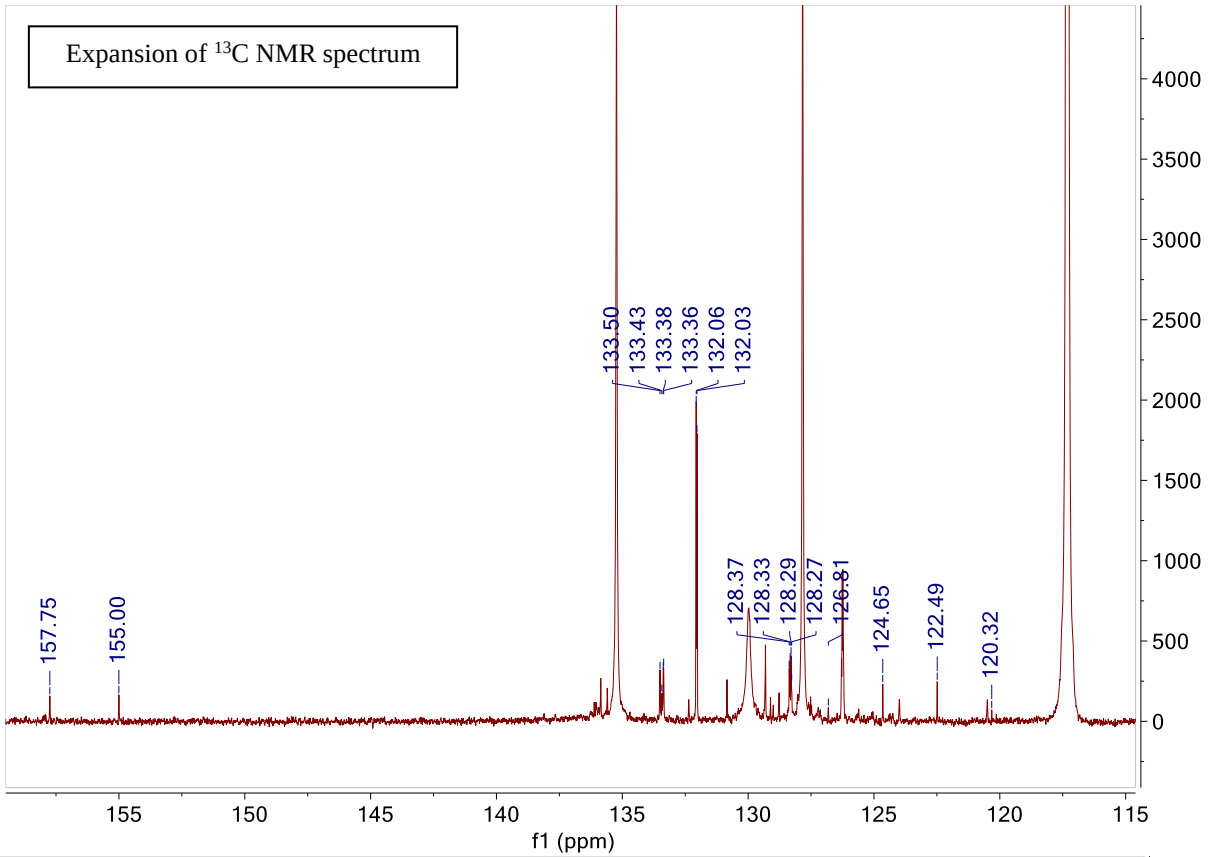


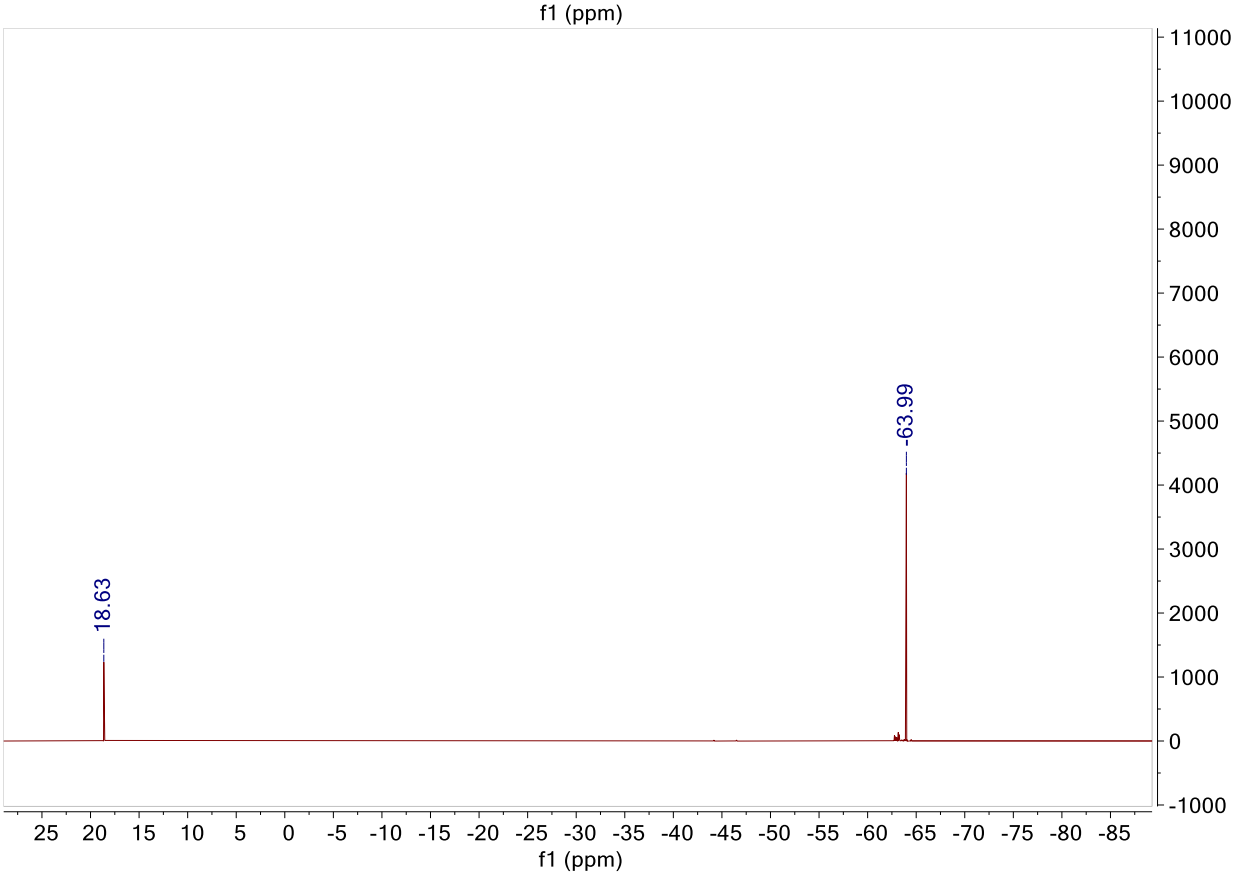

14.48
550
500
450
400
350
300
250
200
150
100
50
0
-50
110
90
70
50
30
10
-10
-30
-50
-70
-90
-110
f1 (ppm)

***In situ* ^{1}H, ^{13}C, and ^{19}F NMR data for 1p.**

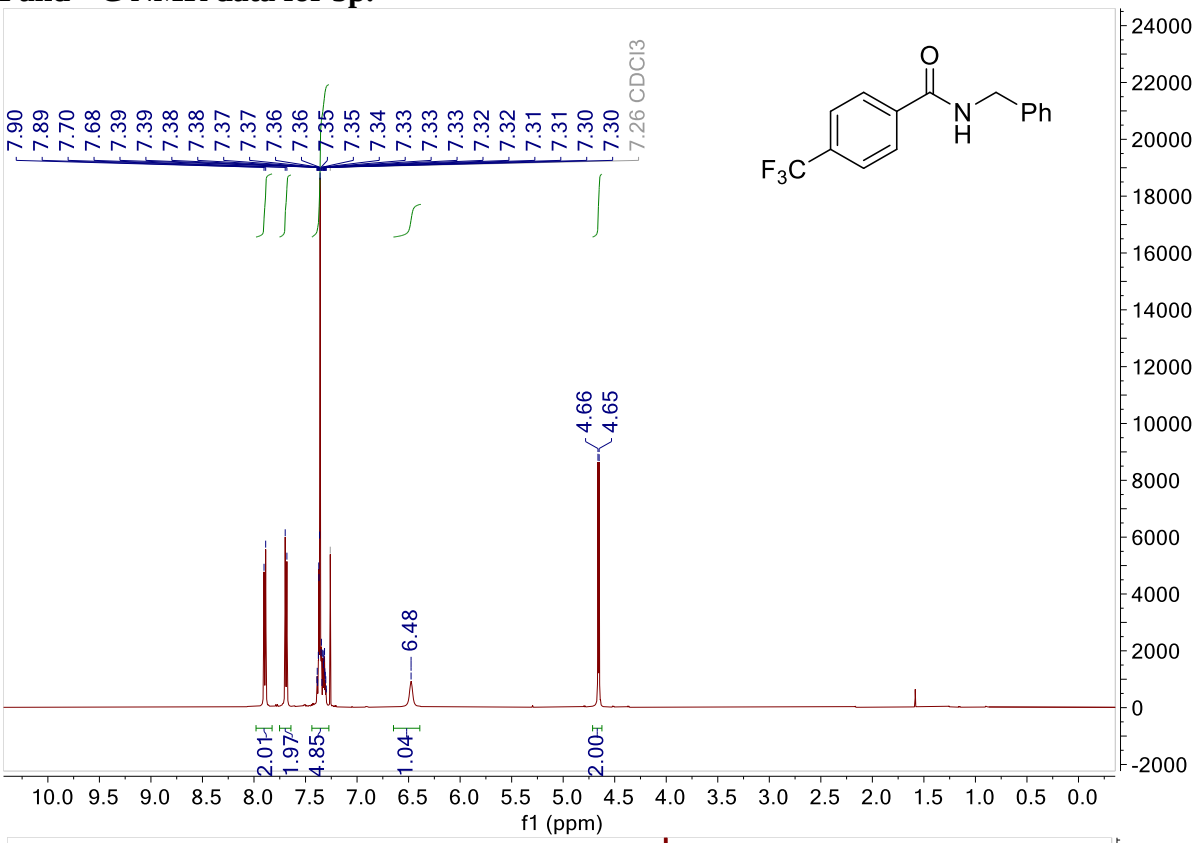


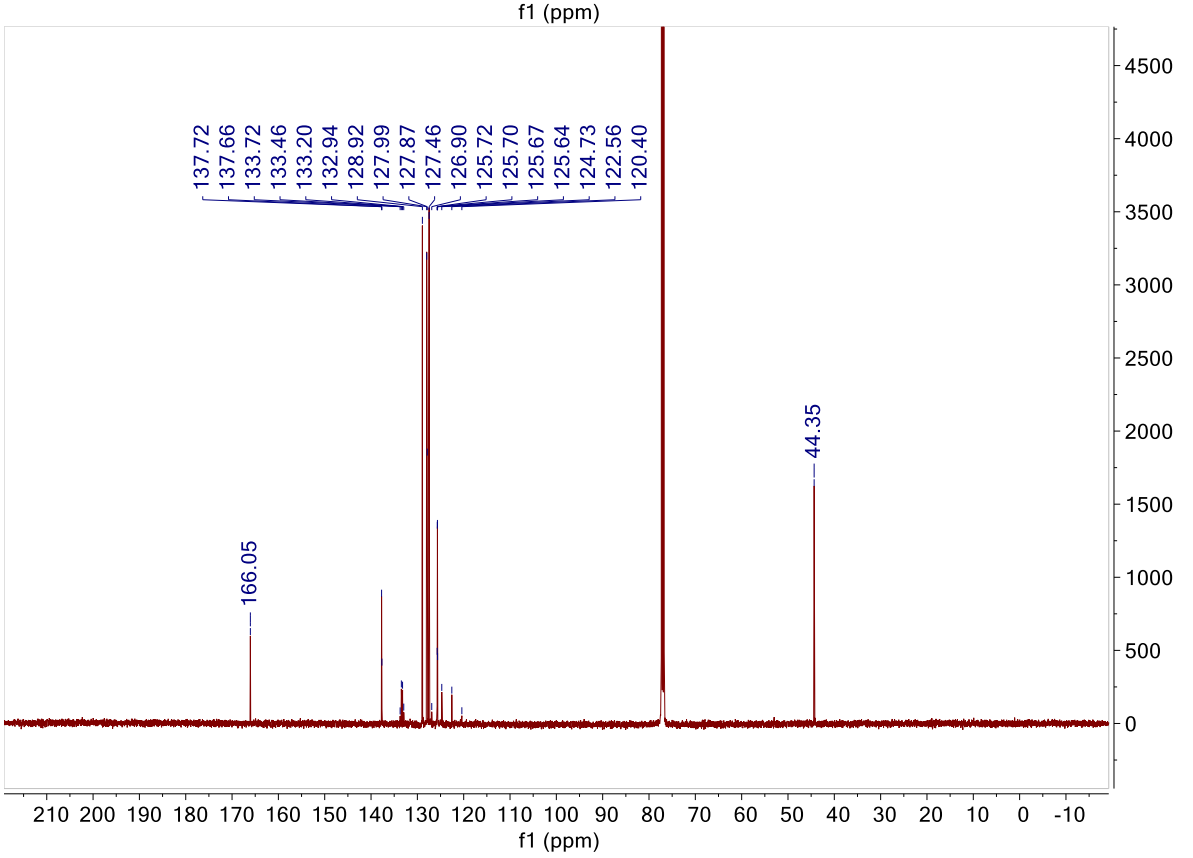


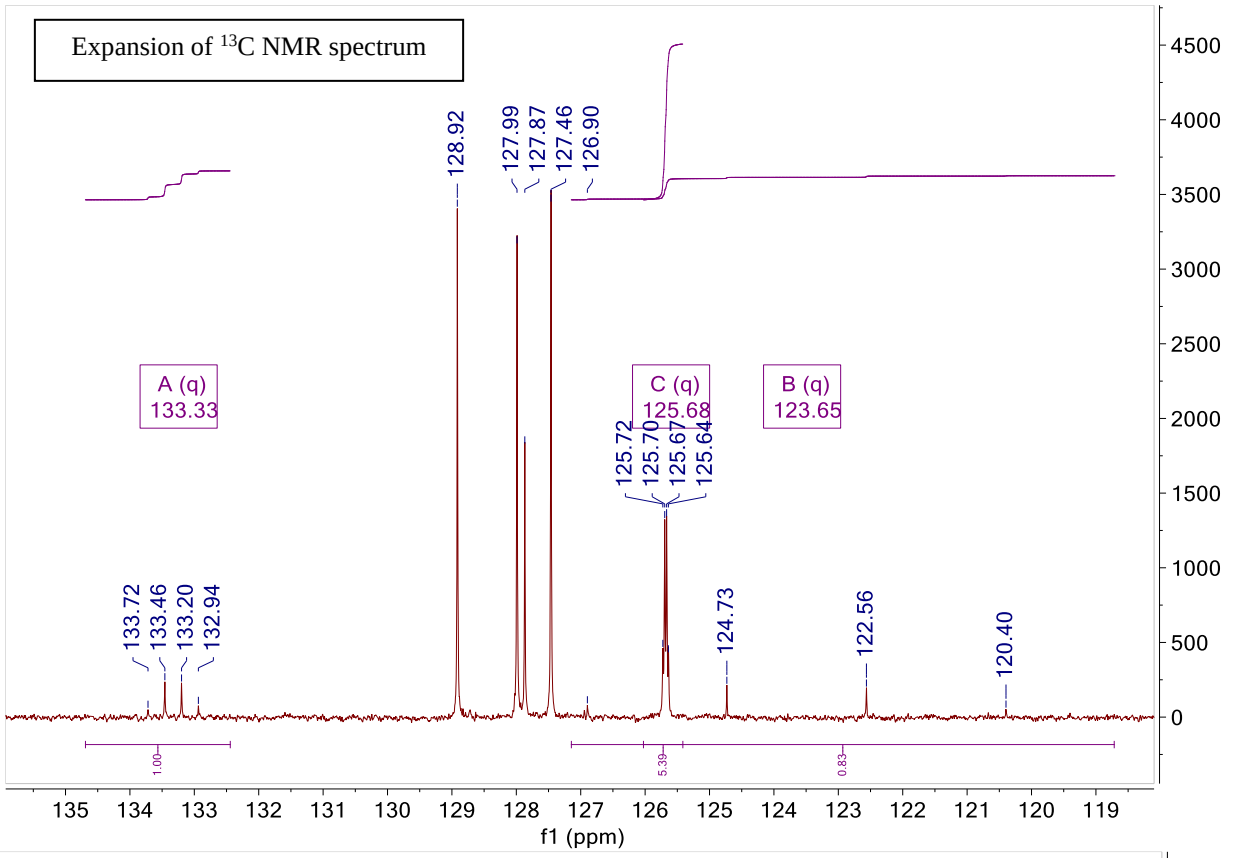

Expansion of ^{13}C NMR spectrum
157.75
155.00
133.50
133.43
133.38
133.36
132.06
132.03
128.37
128.33
128.29
128.27
126.81
124.65
122.49
120.32
4000
3500
3000
2500
2000
1500
1000
500
0
155
150
145
140
135
130
125
120
115
f1 (ppm)

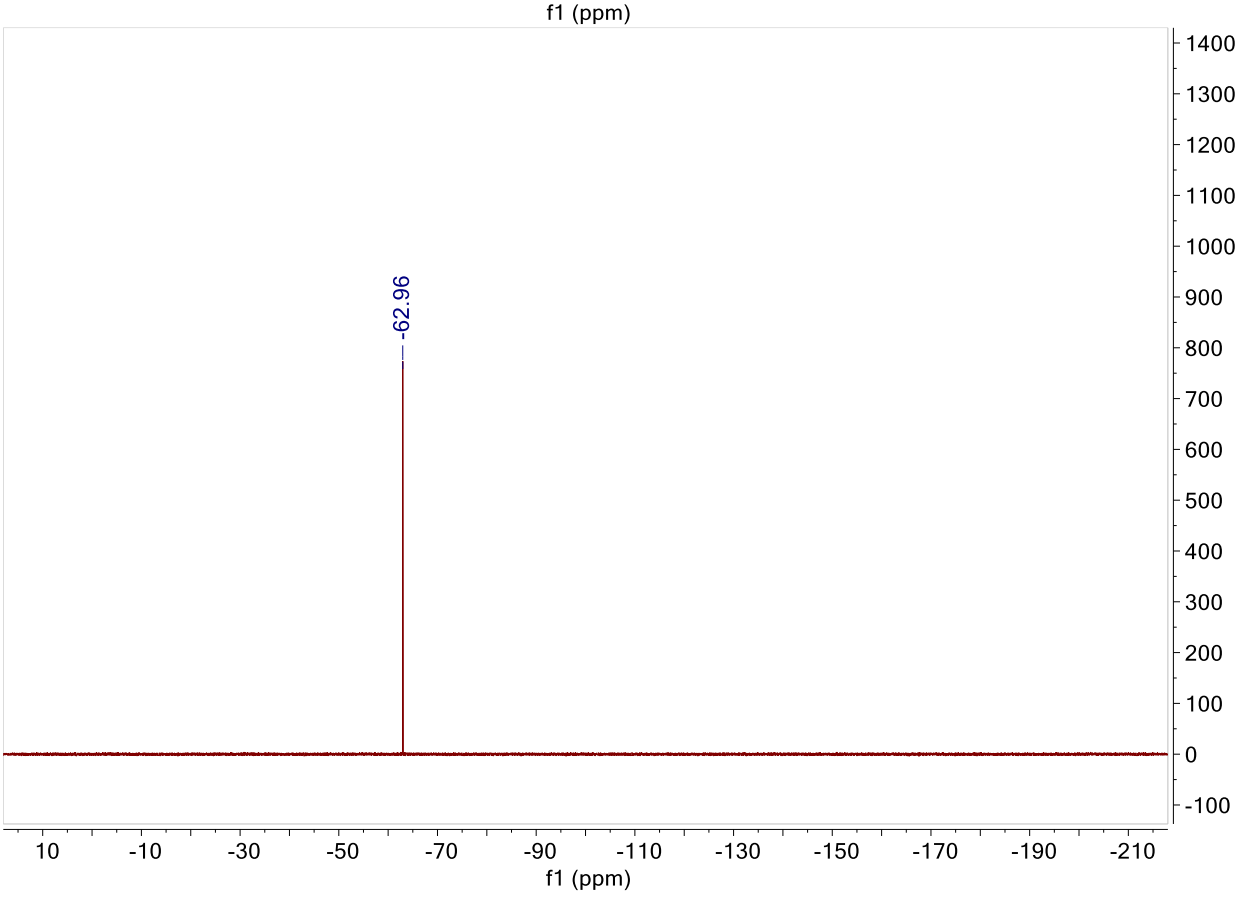

18.63
-63.99
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85
f1 (ppm)

^{1}H and ^{13}C NMR data for 5p.

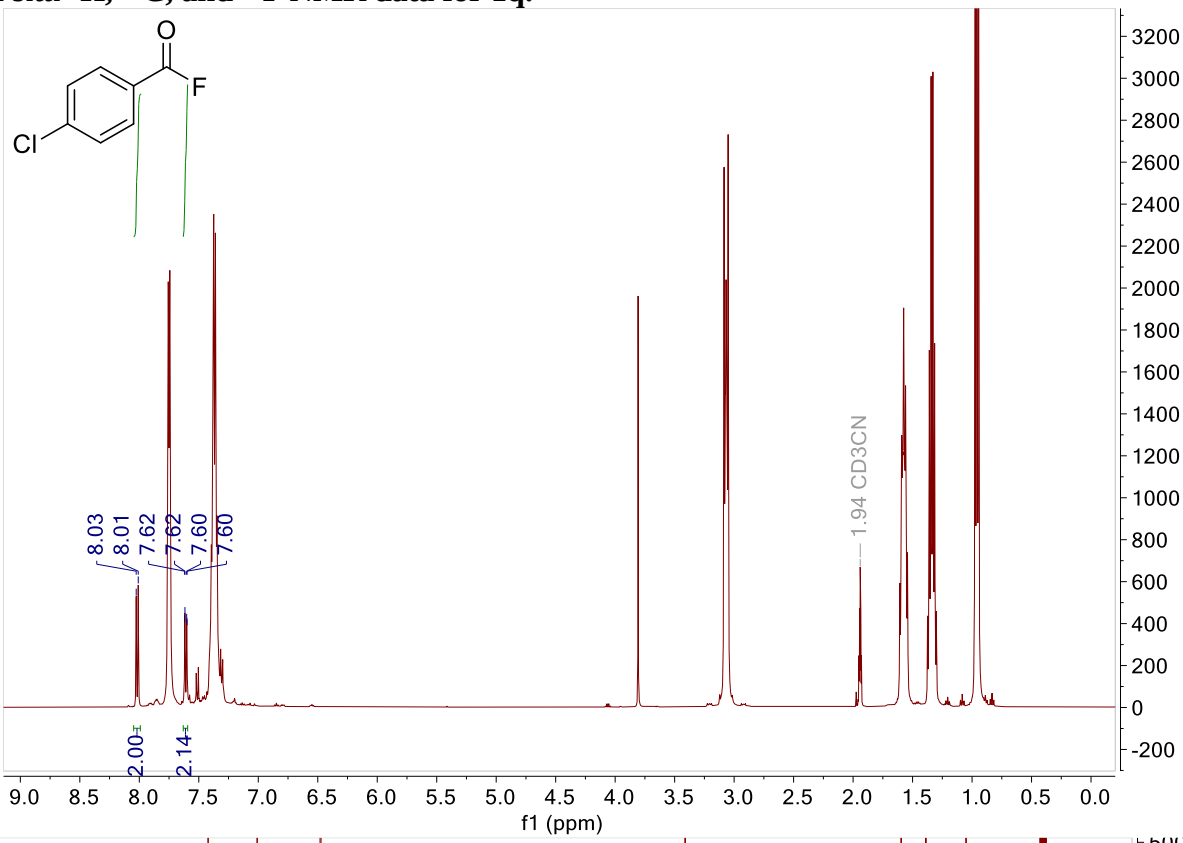


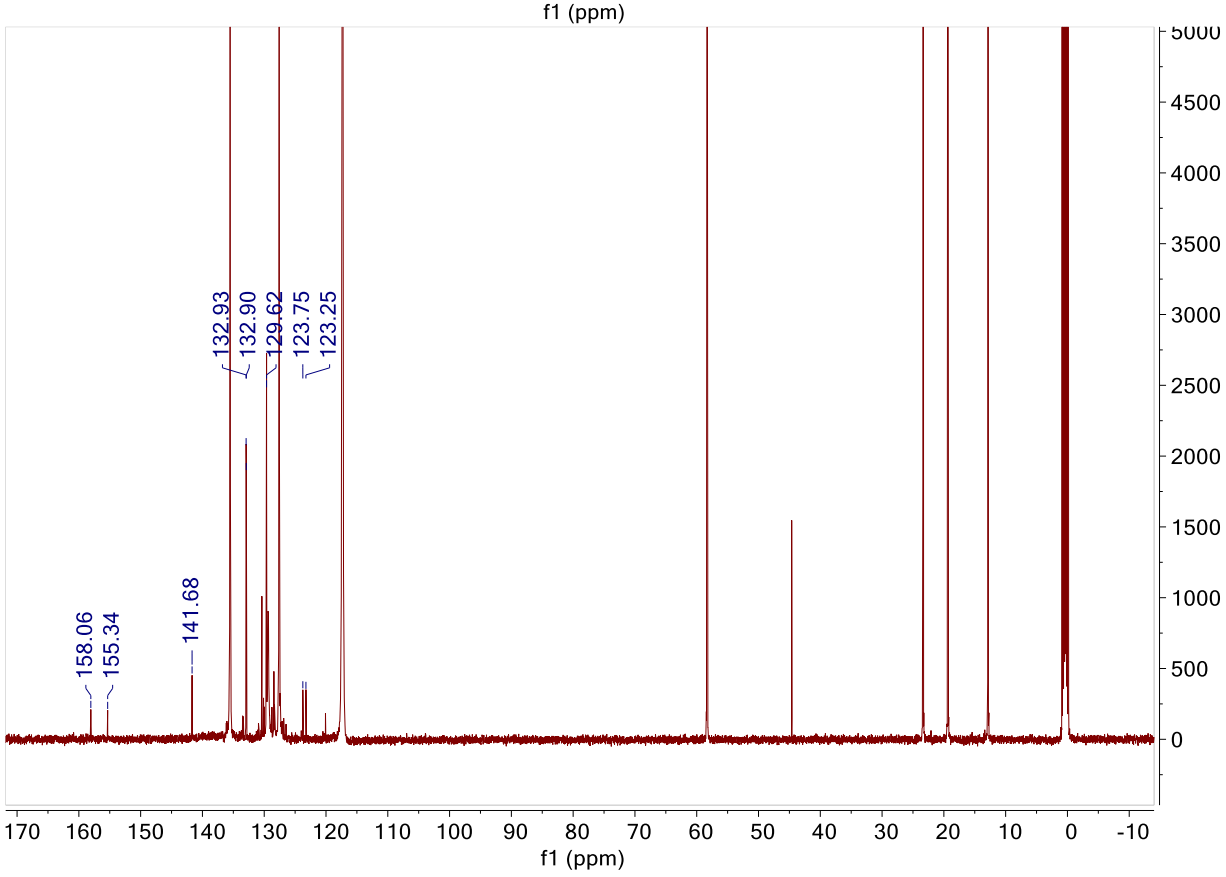


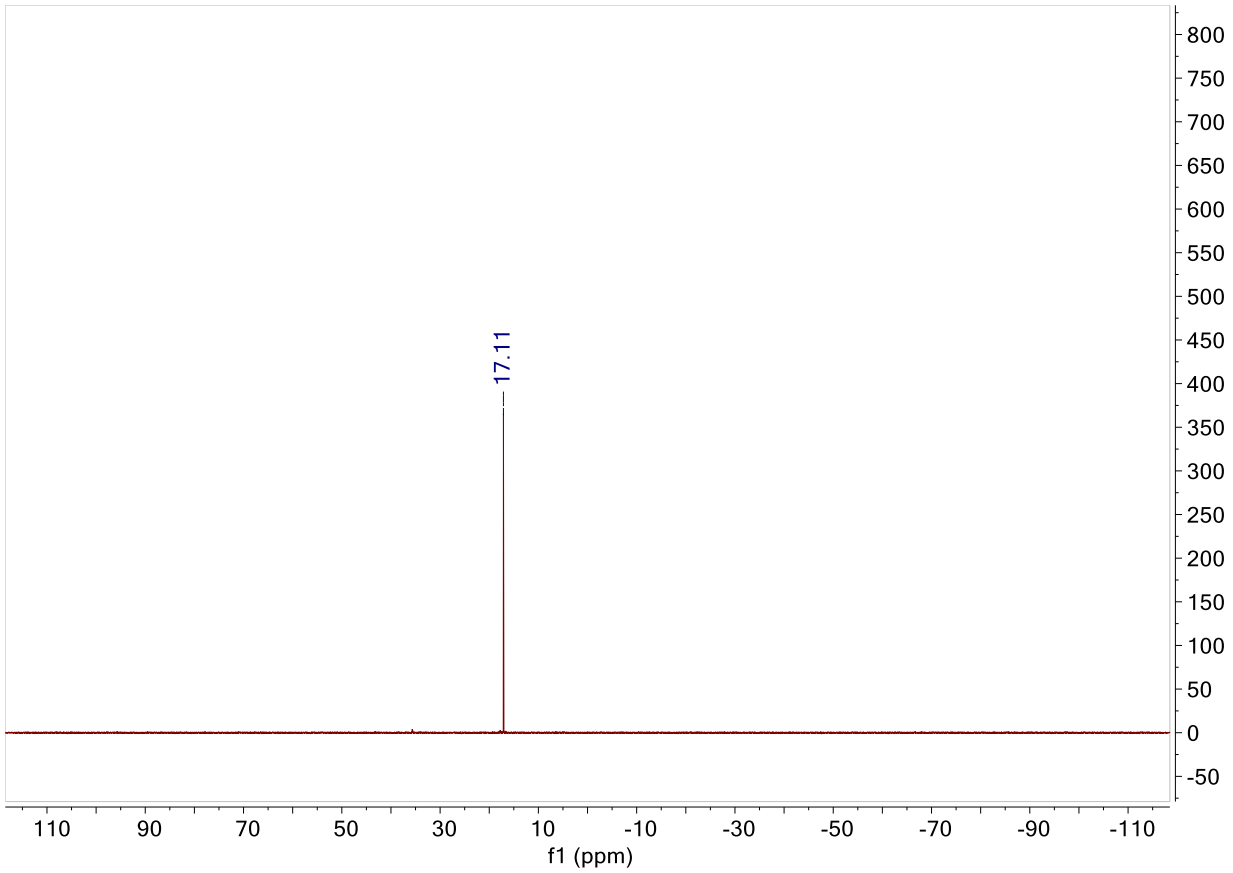

Expansion of ^{13}C NMR spectrum
A (q)
133.33
C (q)
125.68
B (q)
123.65
128.92
127.99
127.87
127.46
126.90
125.72
125.70
125.67
125.64
133.72
133.46
133.20
132.94
124.73
122.56
120.40
1.00
5.39
0.83
f1 (ppm)


-62.96
f1 (ppm)

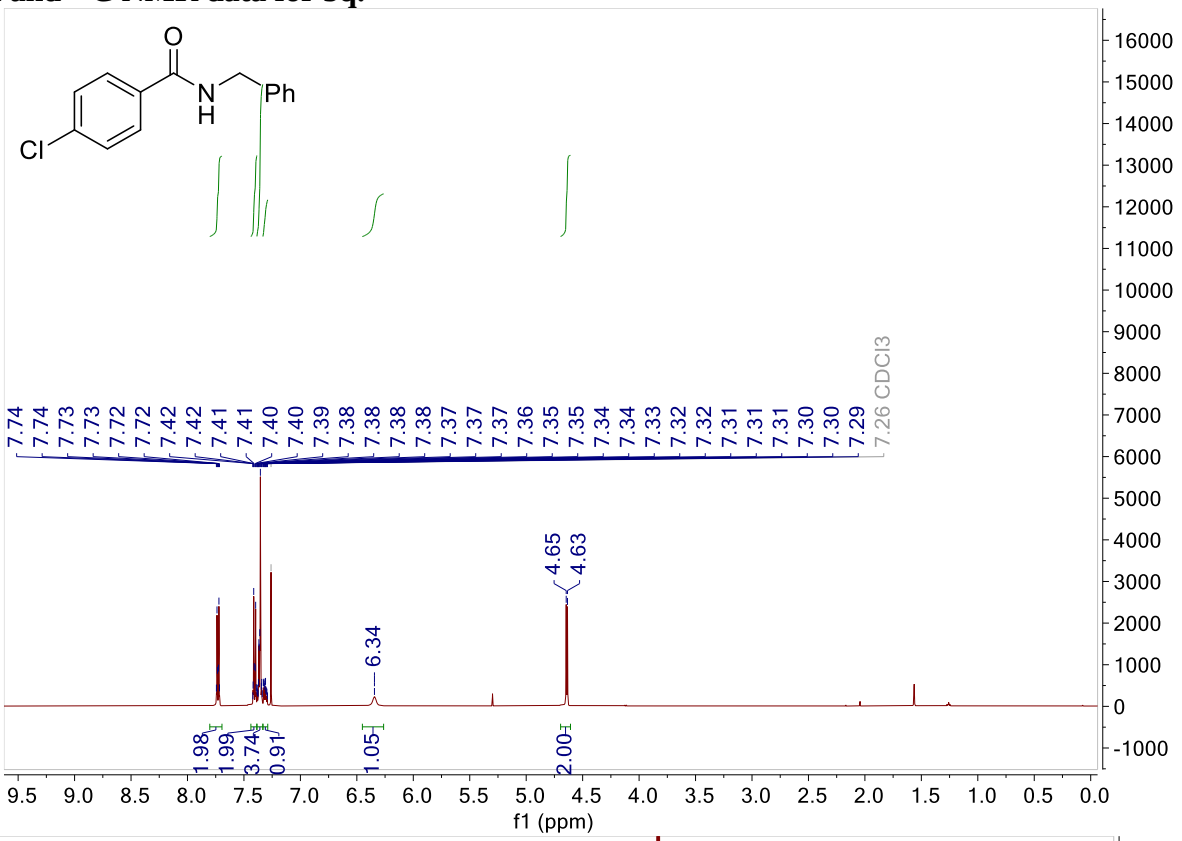
***In situ* ^{1}H, ^{13}C, and ^{19}F NMR data for 1q.**

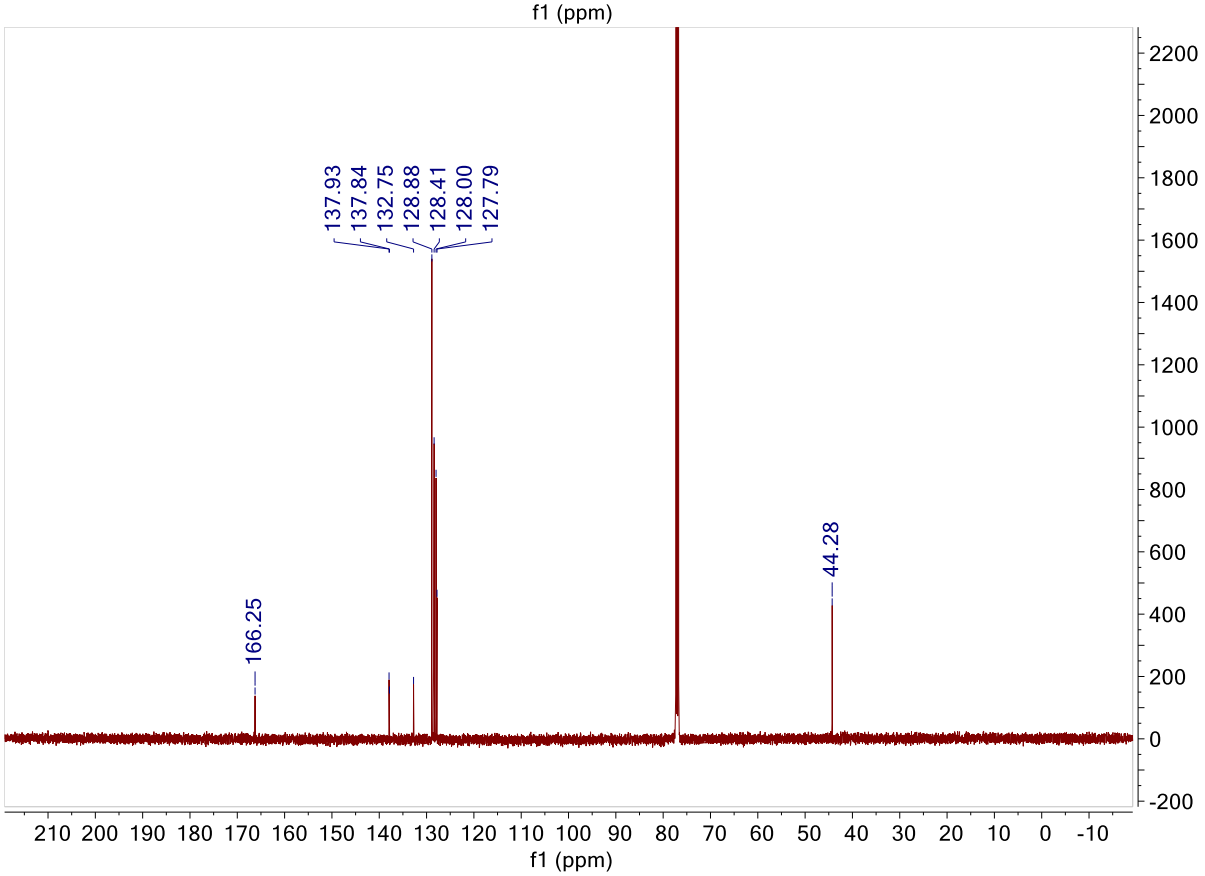




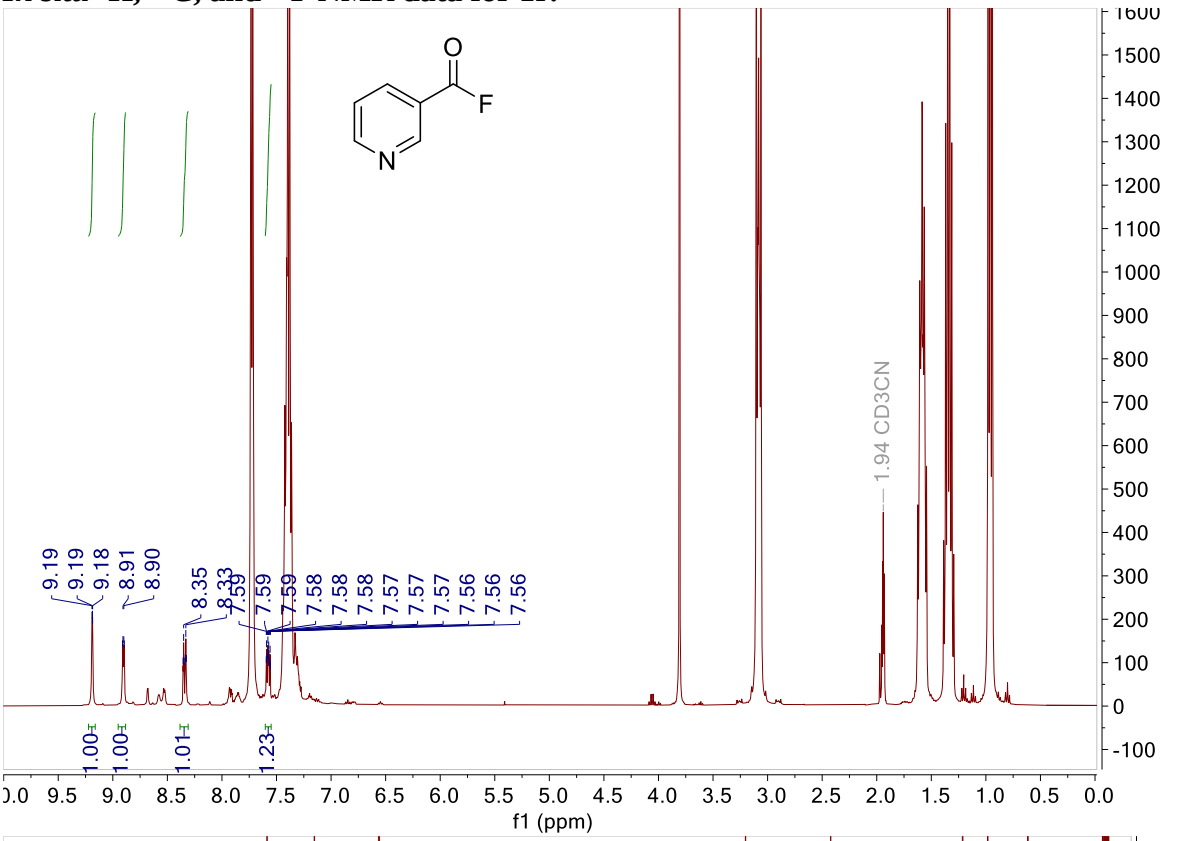

17.11
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
110
90
70
50
30
10
-10
-30
-50
-70
-90
-110
f1 (ppm)

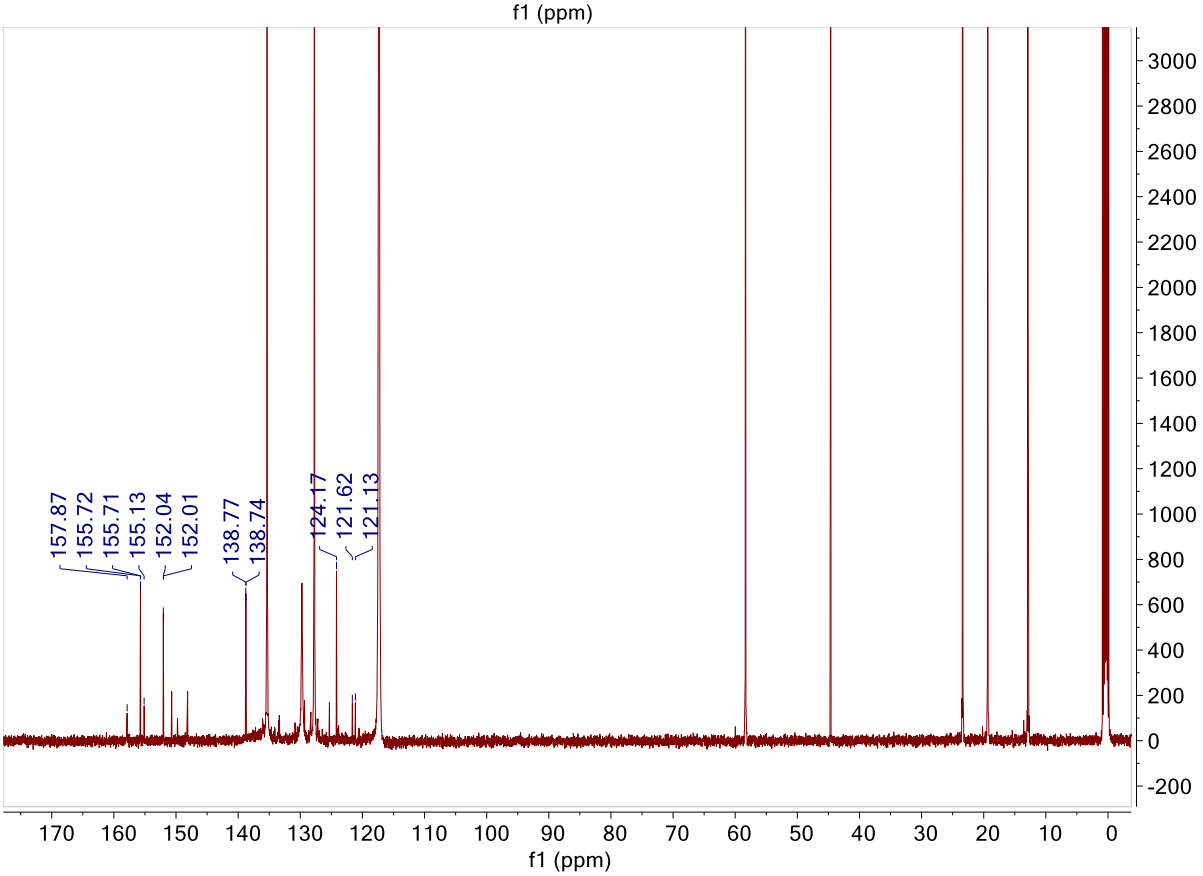
^{1}H and ^{13}C NMR data for 5q.

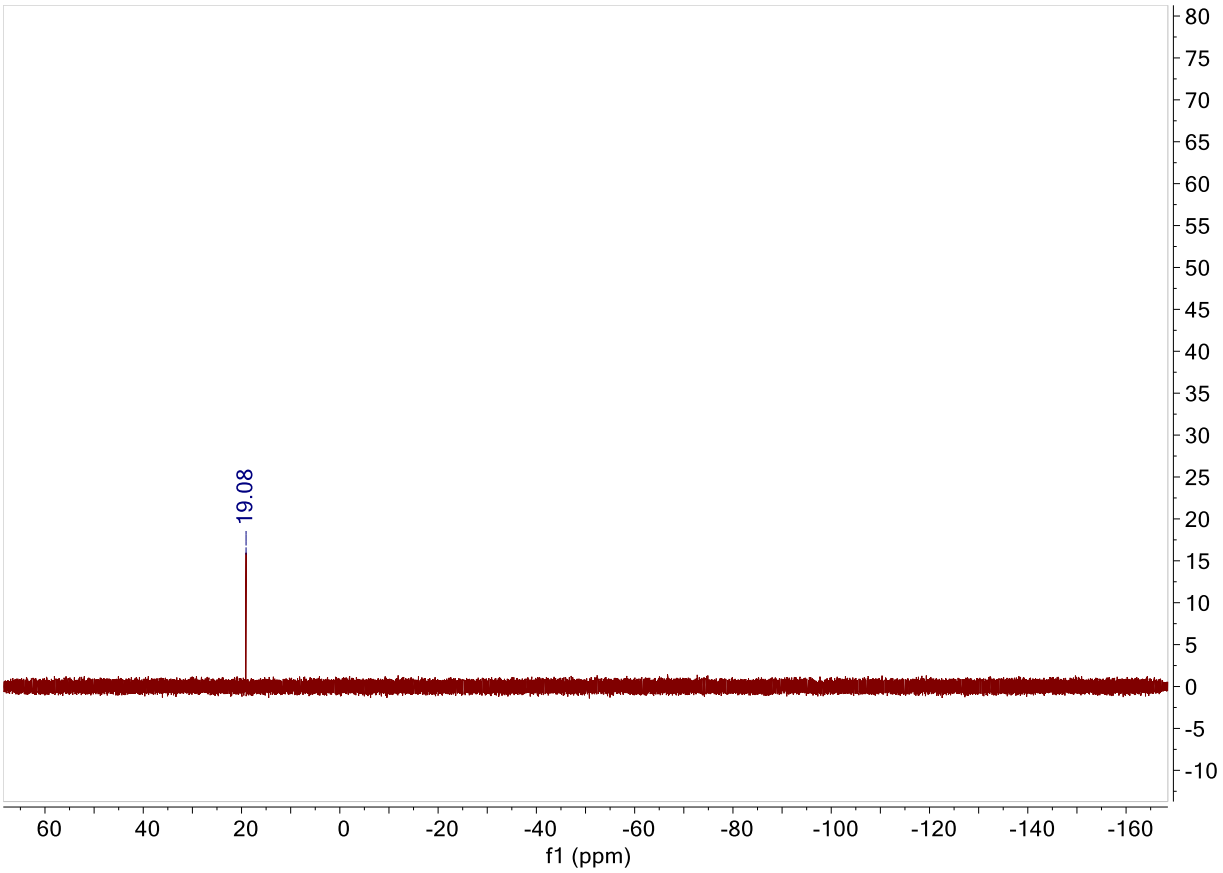




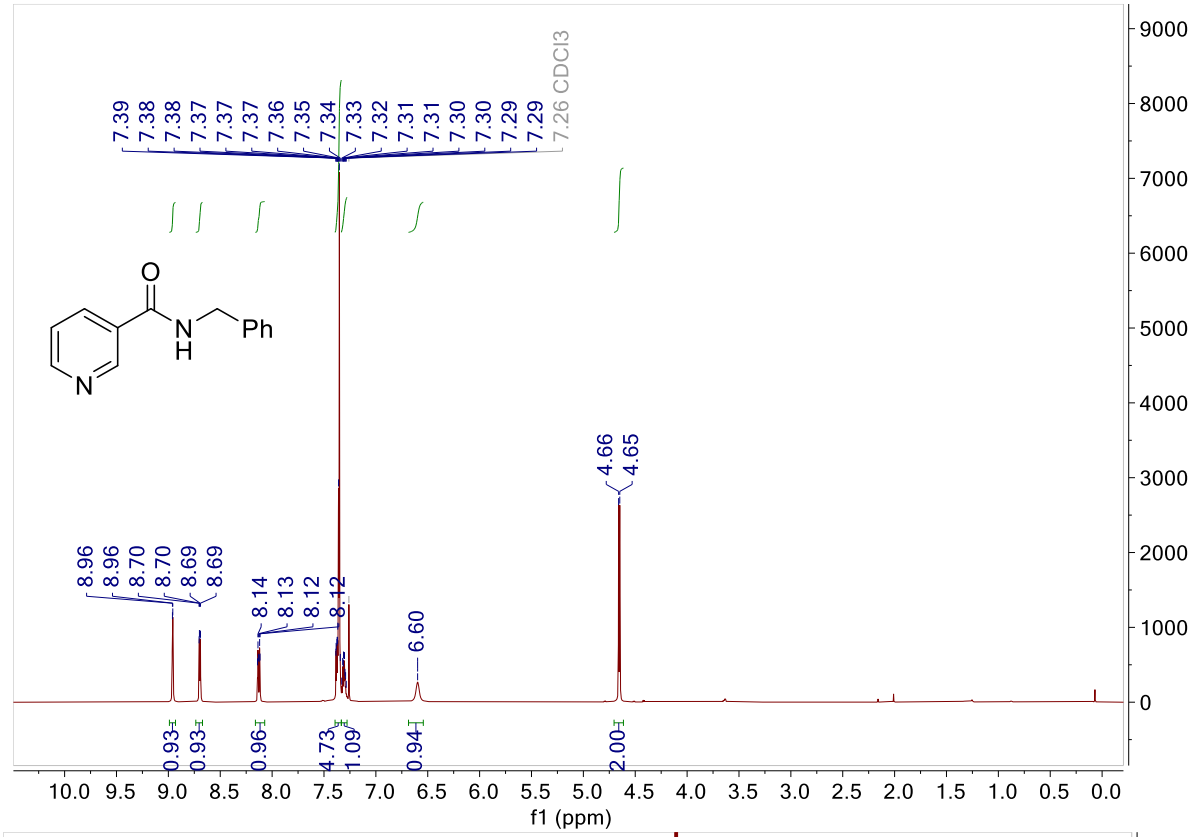
***In situ* ^{1}H, ^{13}C, and ^{19}F NMR data for 1r.**

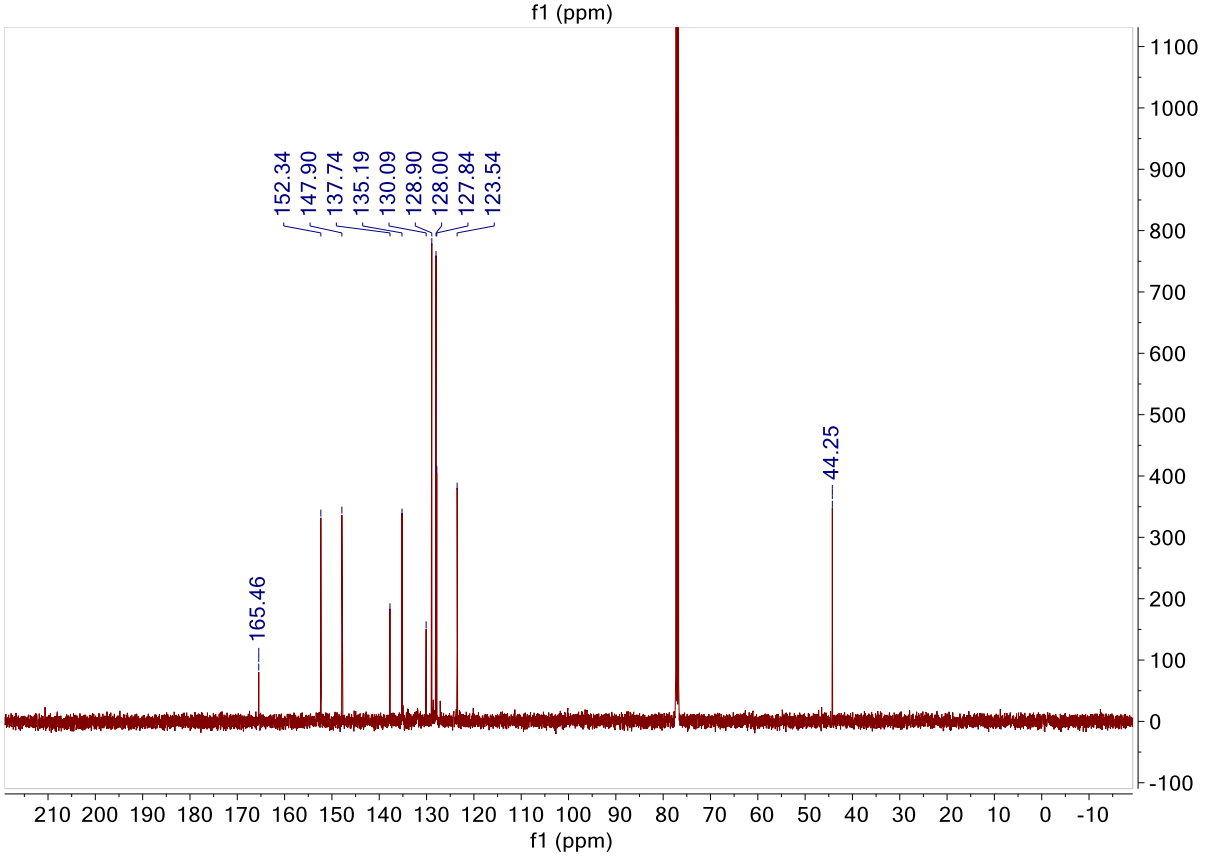




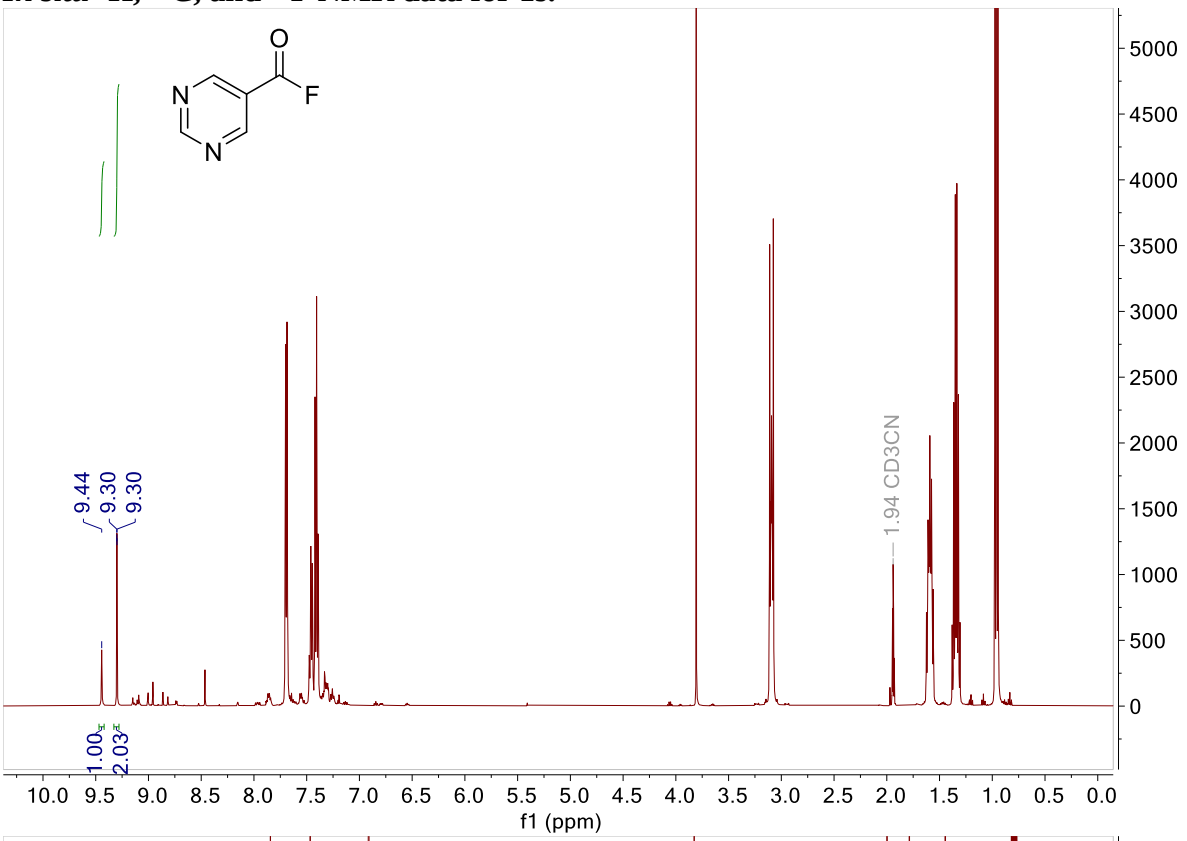

19.08
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
-10
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
f1 (ppm)

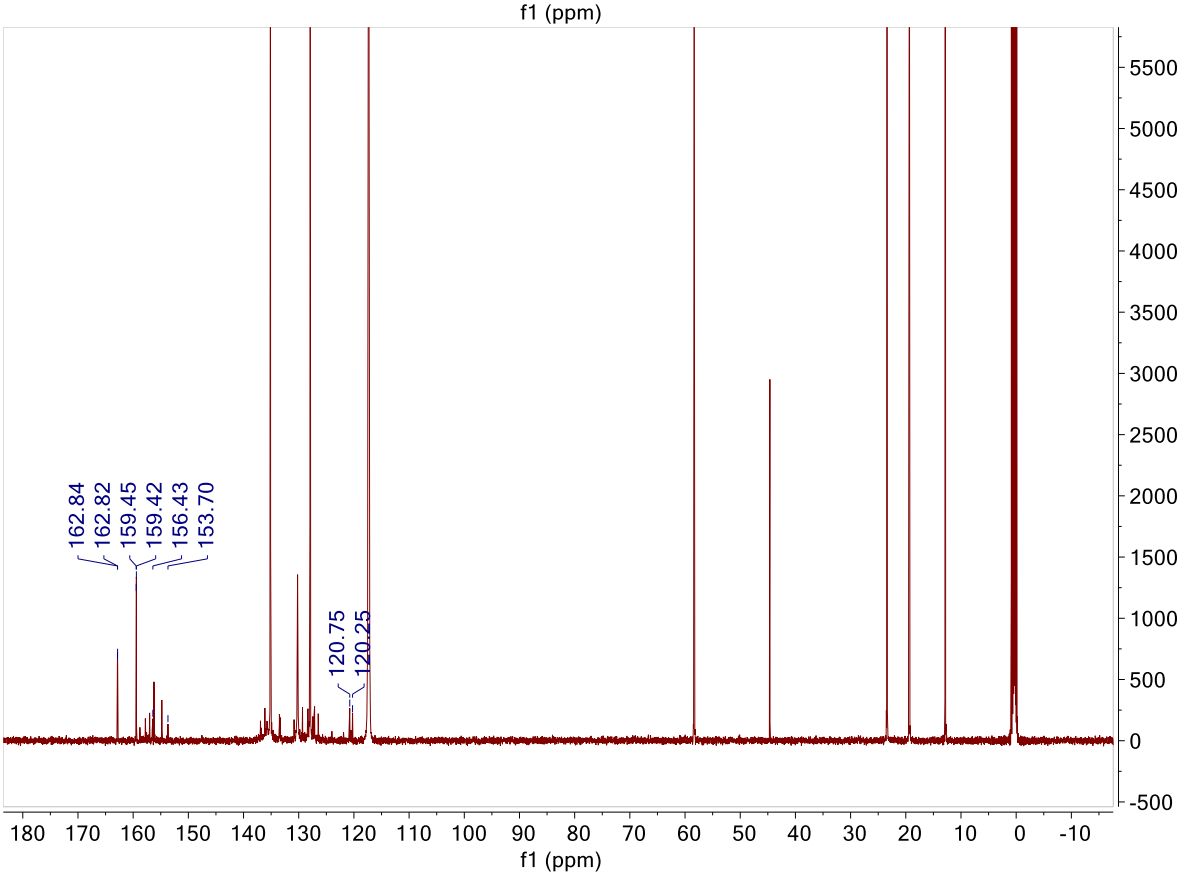
^{1}H and ^{13}C NMR data for 5r.

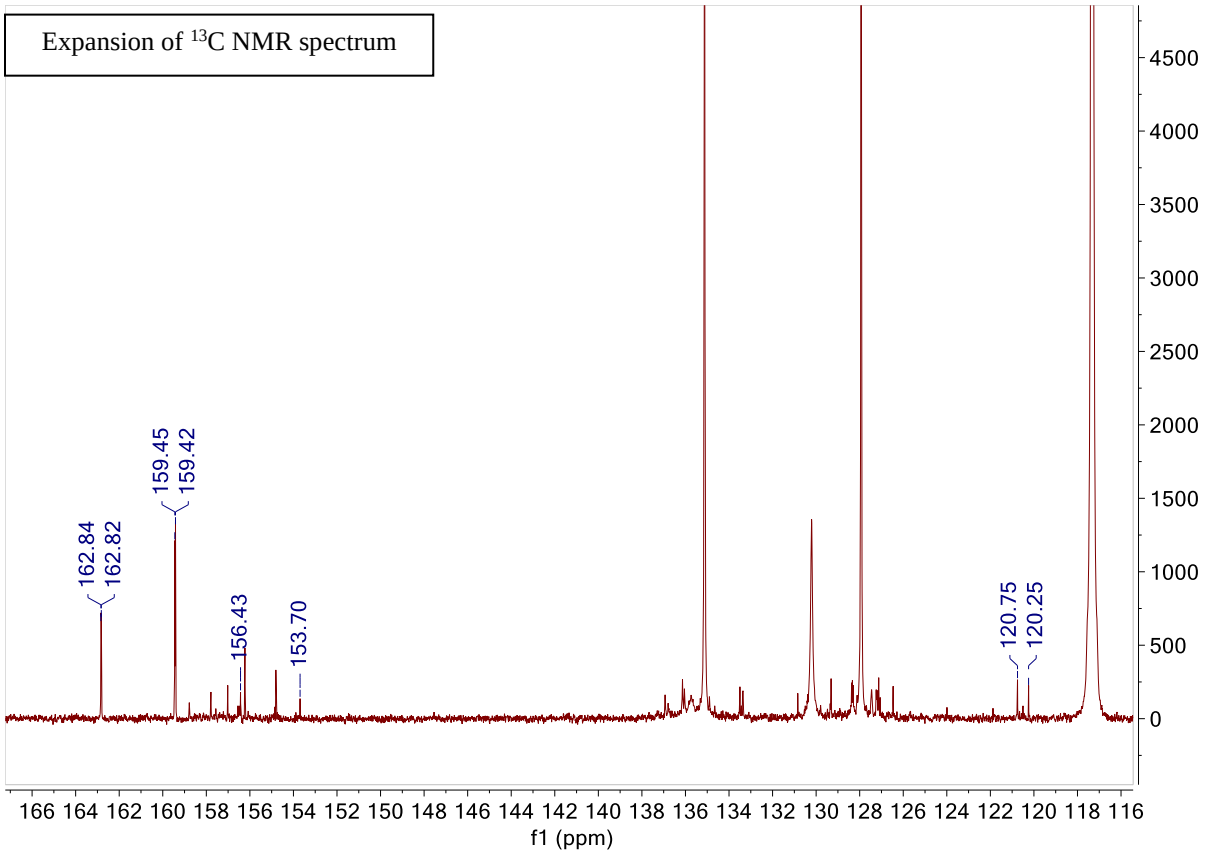


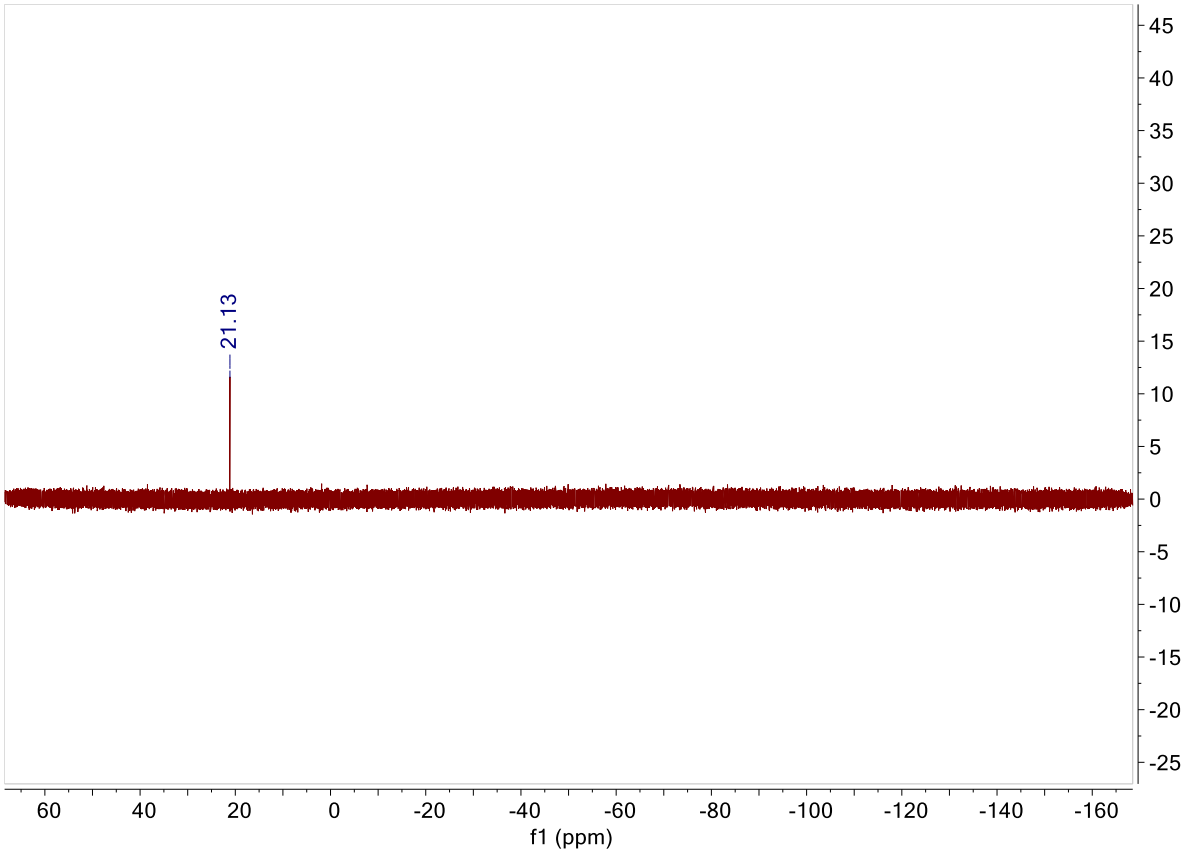


***In situ* ^{1}H, ^{13}C, and ^{19}F NMR data for 1s.**

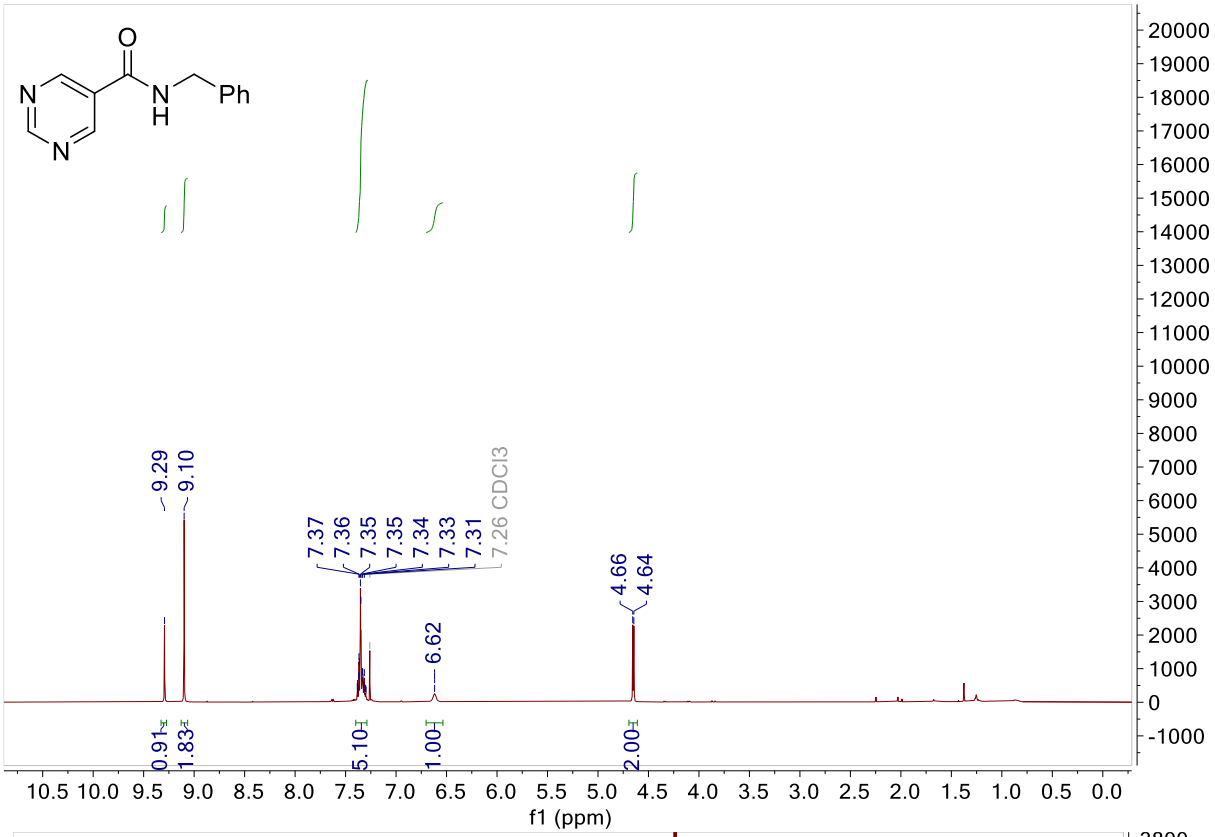


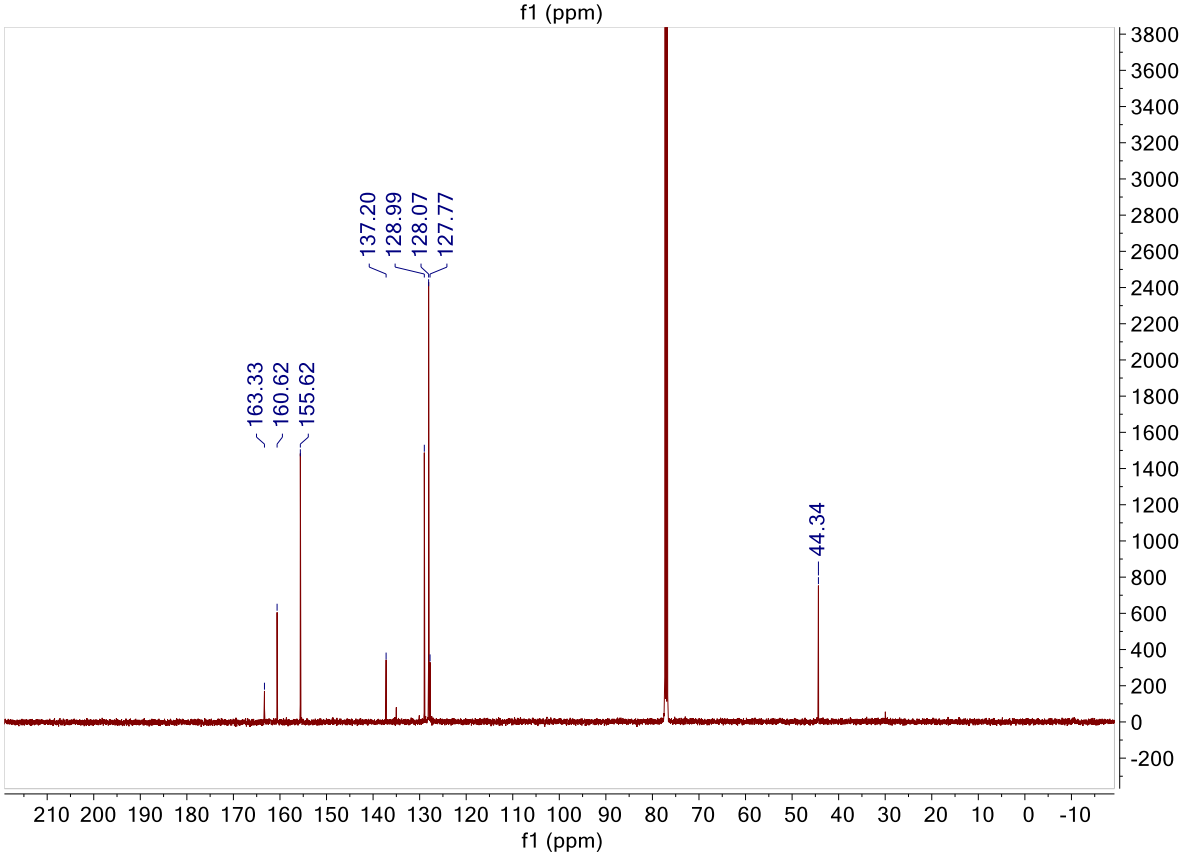



Expansion of ^{13}C NMR spectrum
162.84
162.82
159.45
159.42
156.43
153.70
120.75
120.25
4500
4000
3500
3000
2500
2000
1500
1000
500
0
166 164 162 160 158 156 154 152 150 148 146 144 142 140 138 136 134 132 130 128 126 124 122 120 118 116
f1 (ppm)

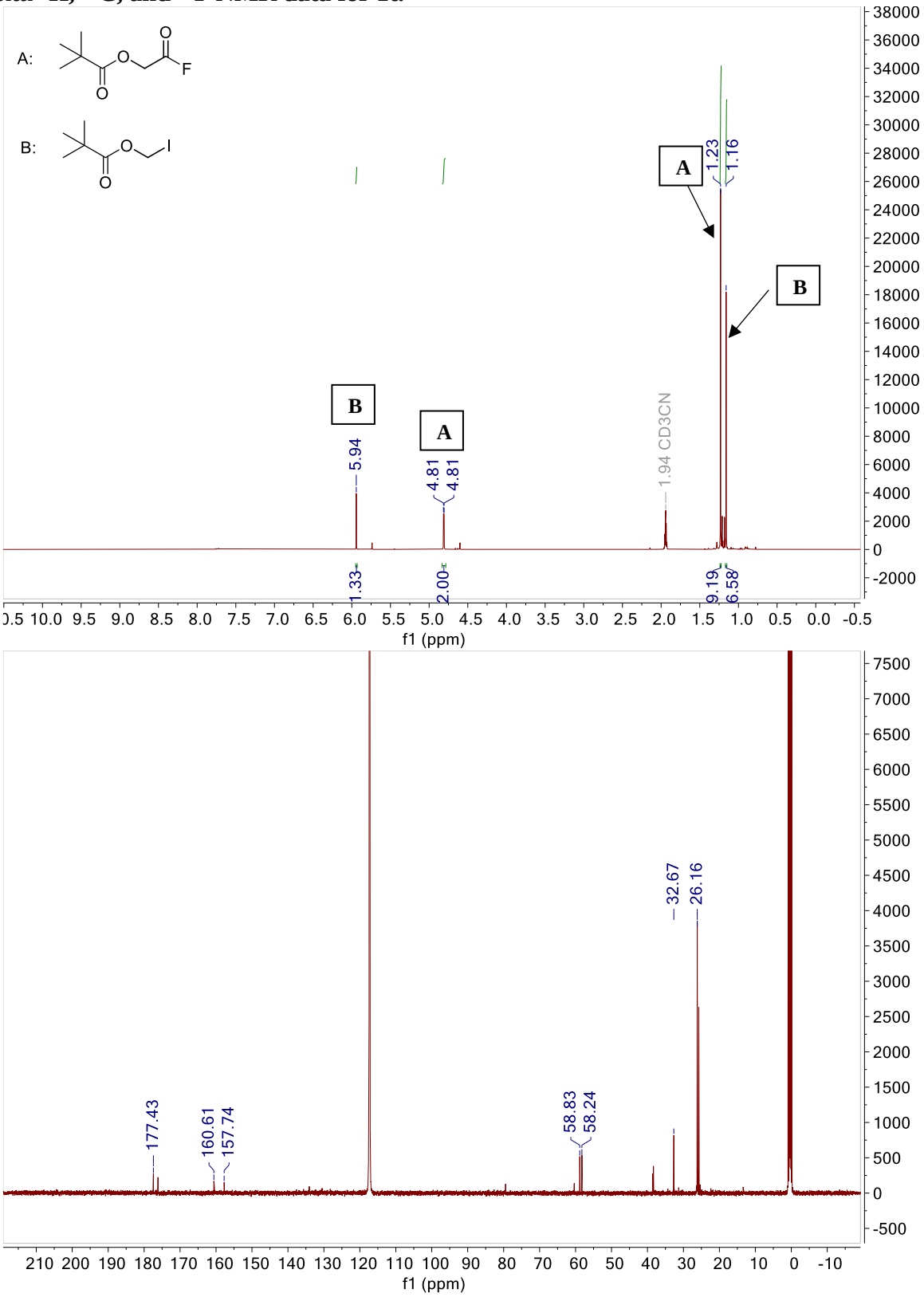

21.13
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160
f1 (ppm)

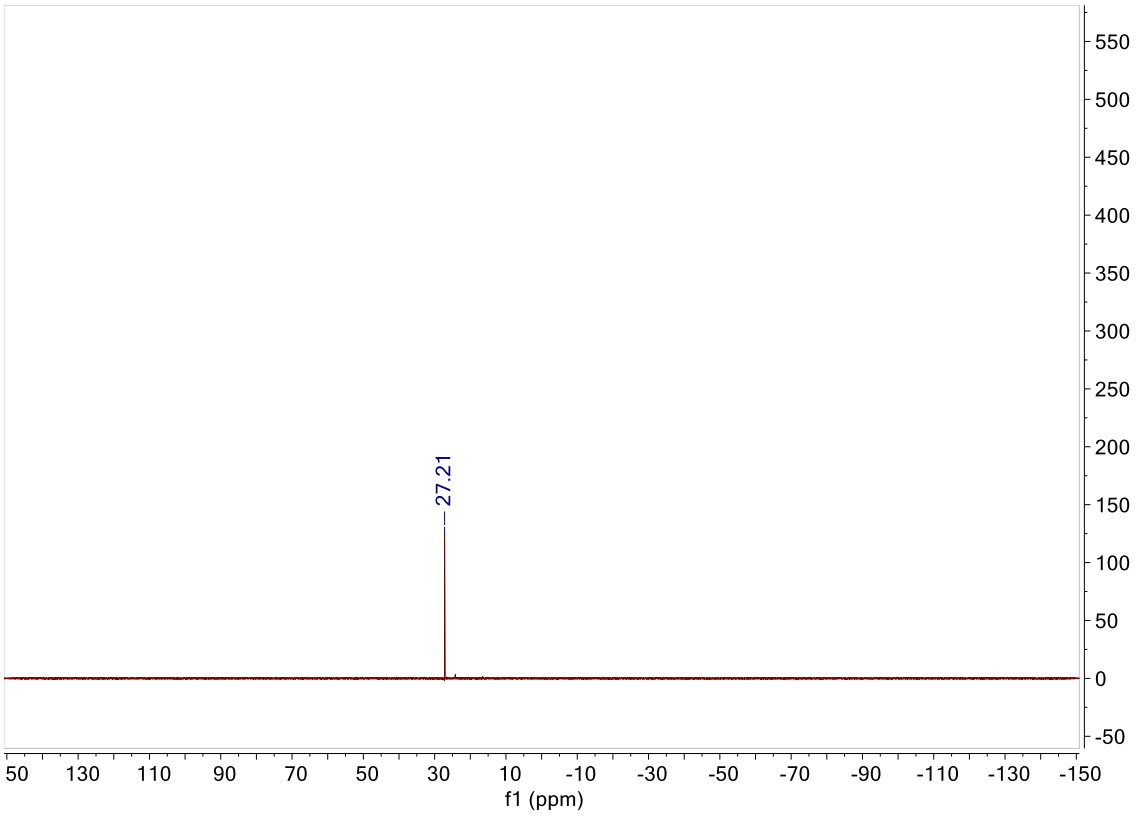
^{1}H and ^{13}C NMR data for 5s.



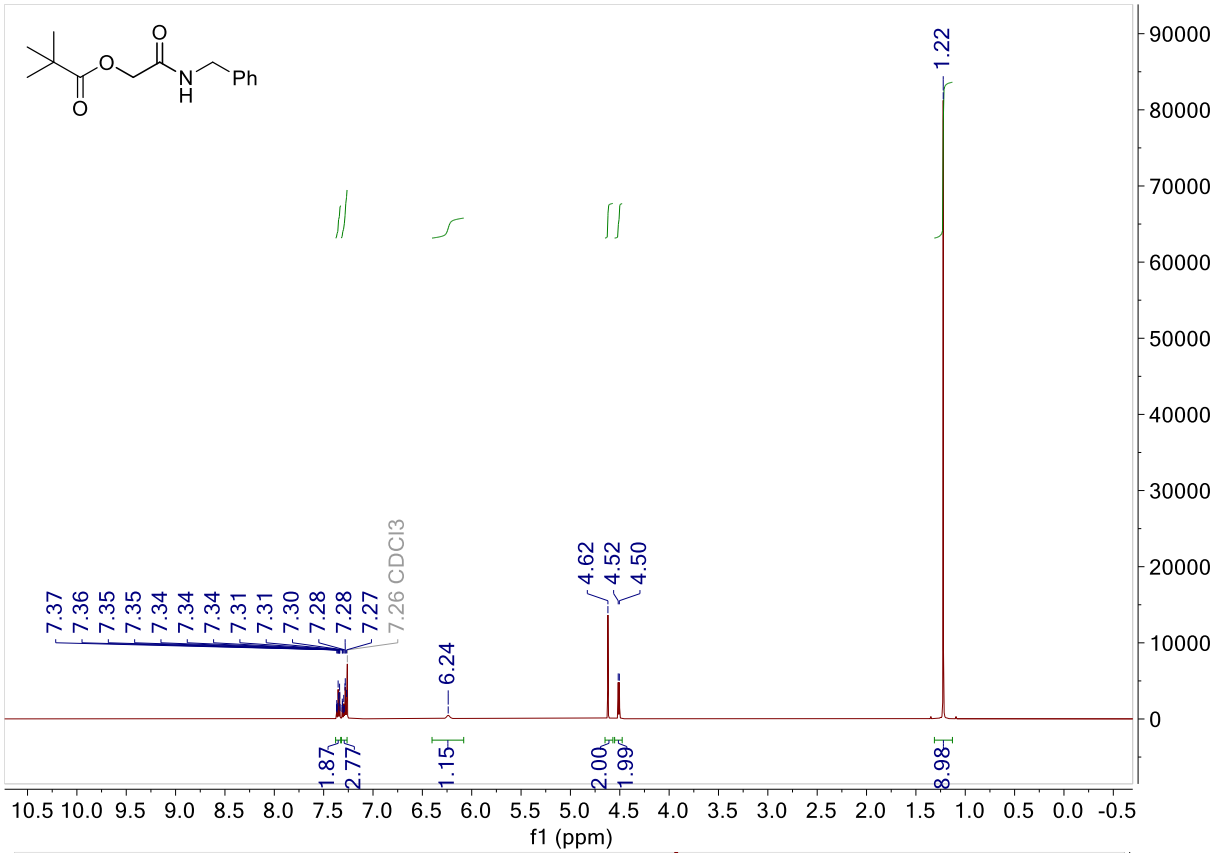


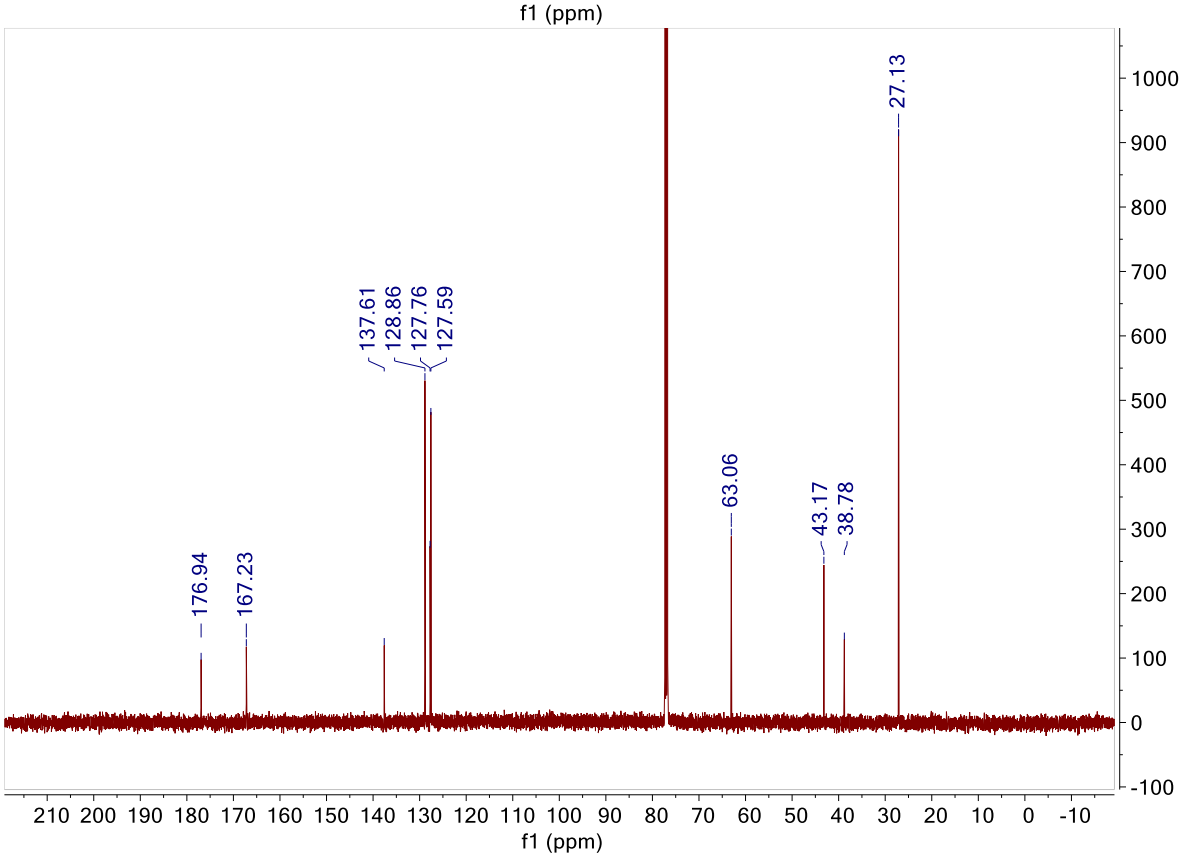
***In situ* ^{1}H, ^{13}C, and ^{19}F NMR data for 1t.**



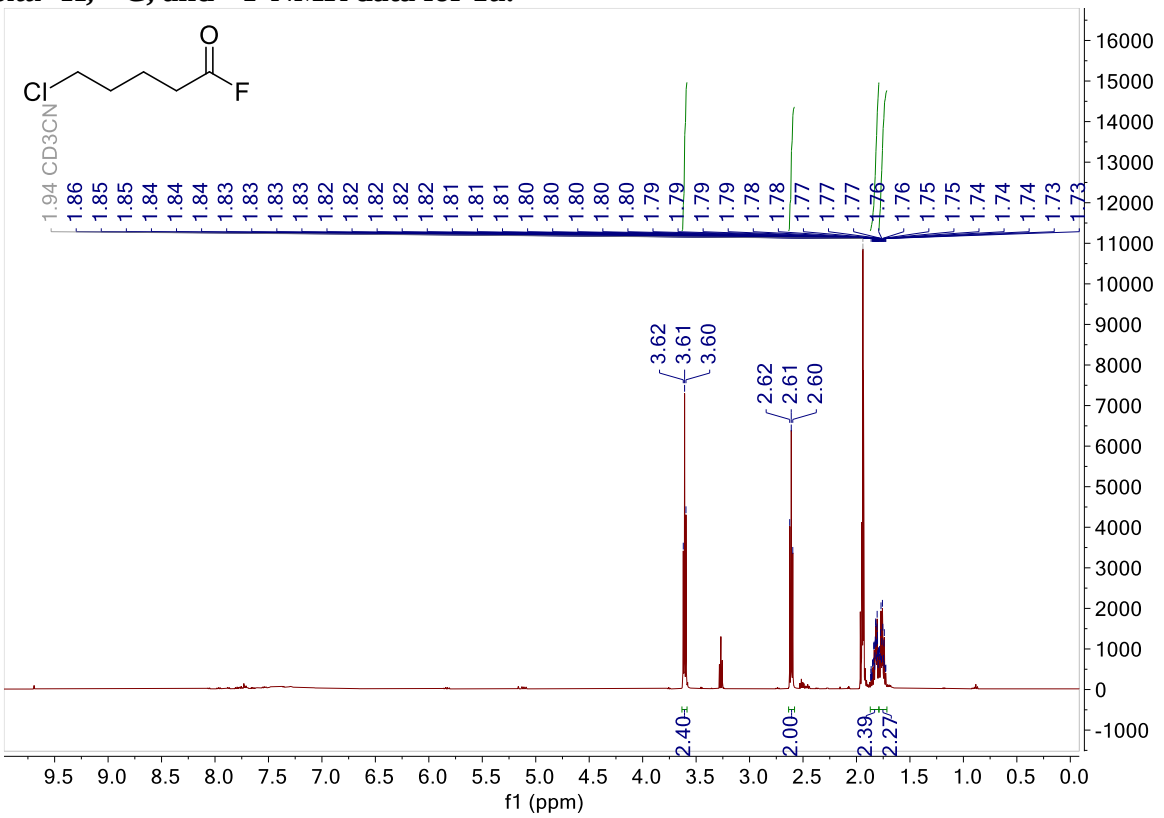

27.21
550
500
450
400
350
300
250
200
150
100
50
0
-50
50
130
110
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
f1 (ppm)

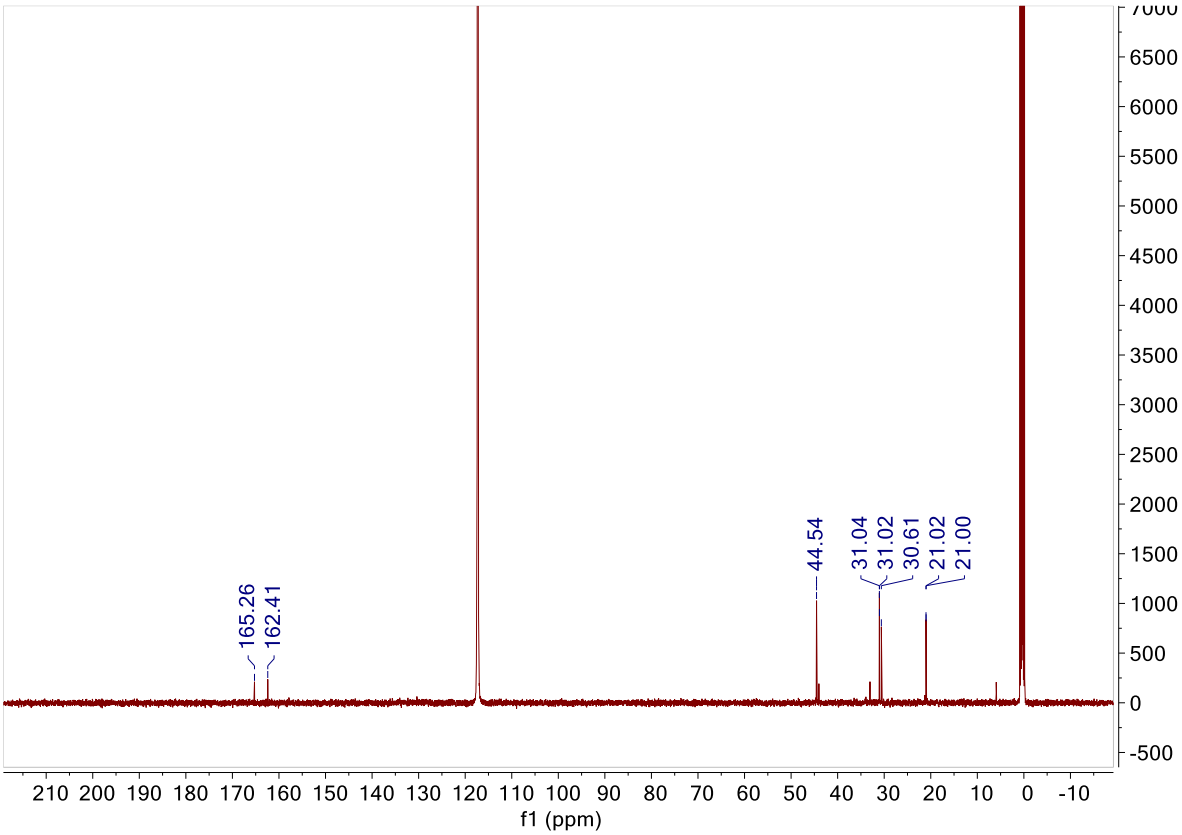
^{1}H and ^{13}C NMR data for 5t.

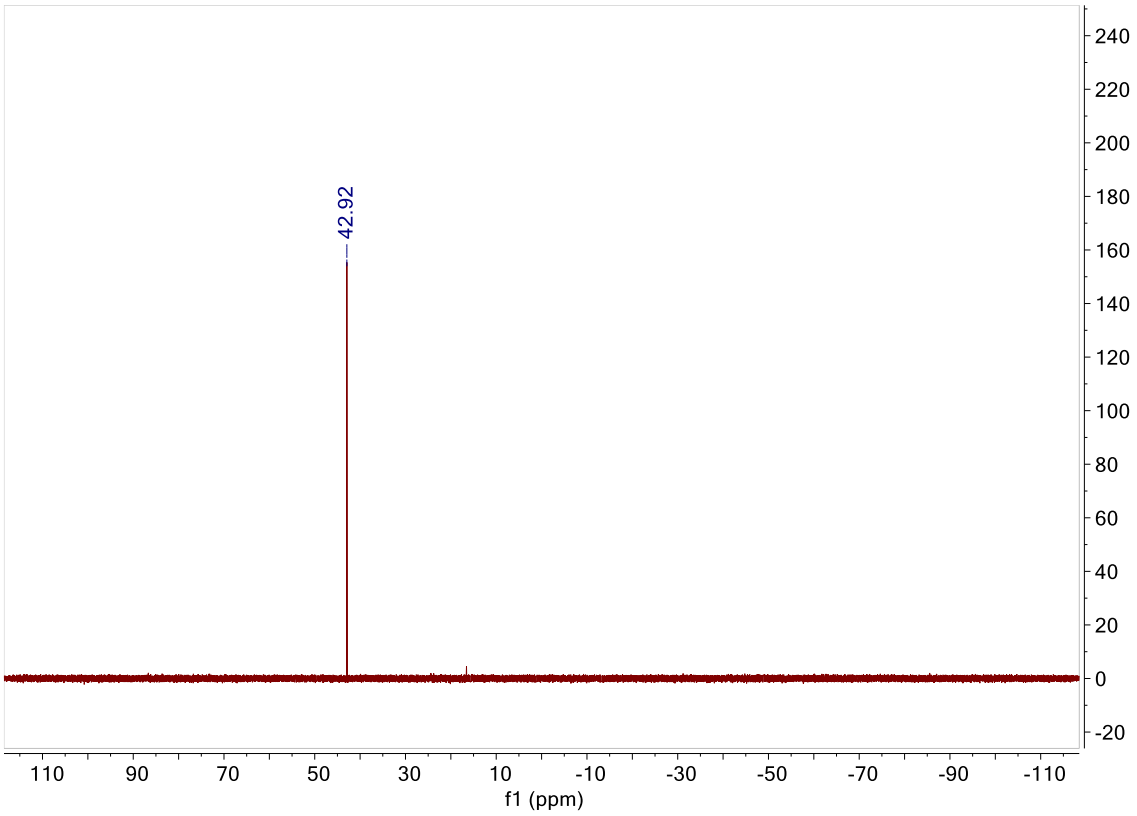




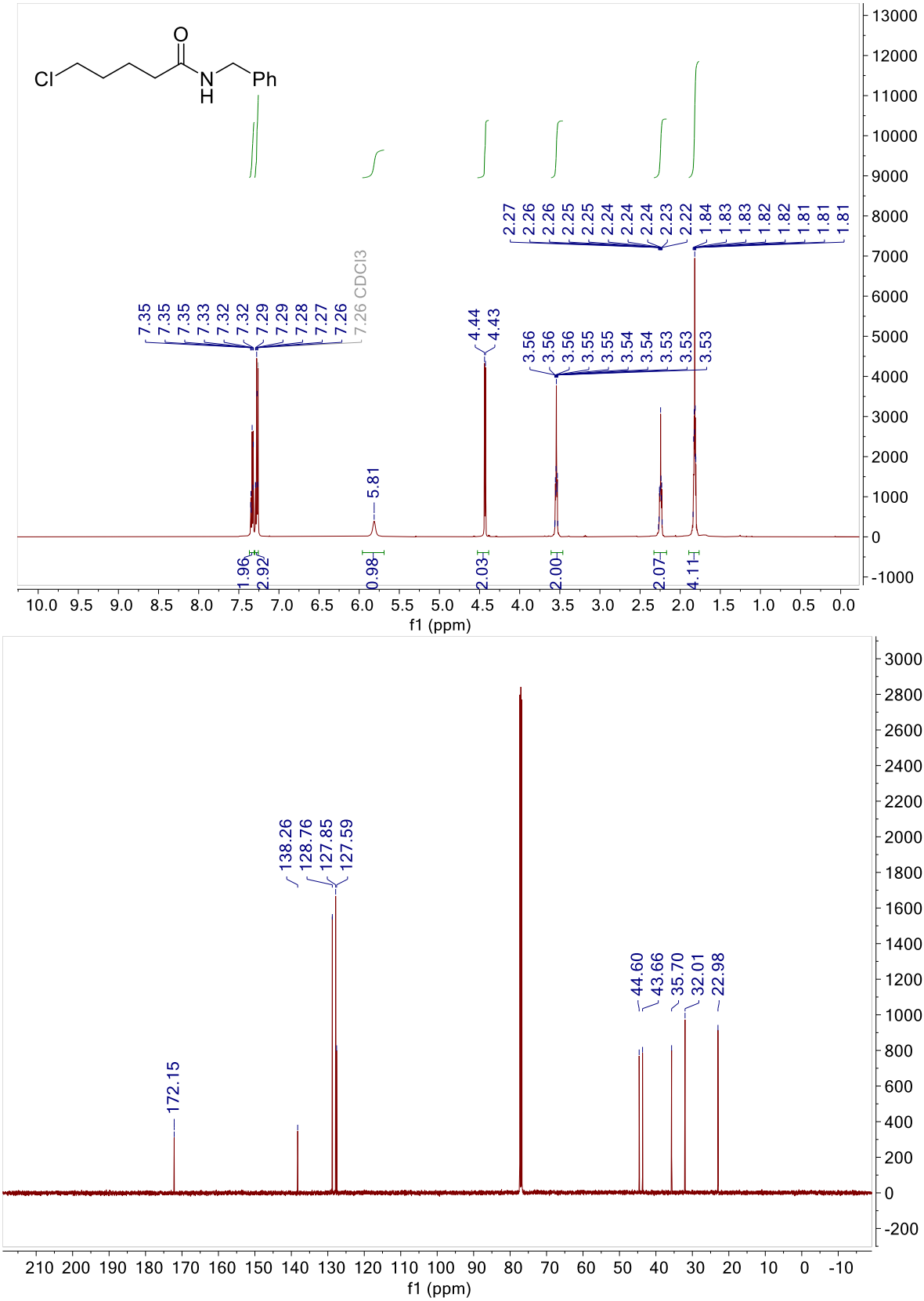
***In situ* ^{1}H, ^{13}C, and ^{19}F NMR data for 1u.**



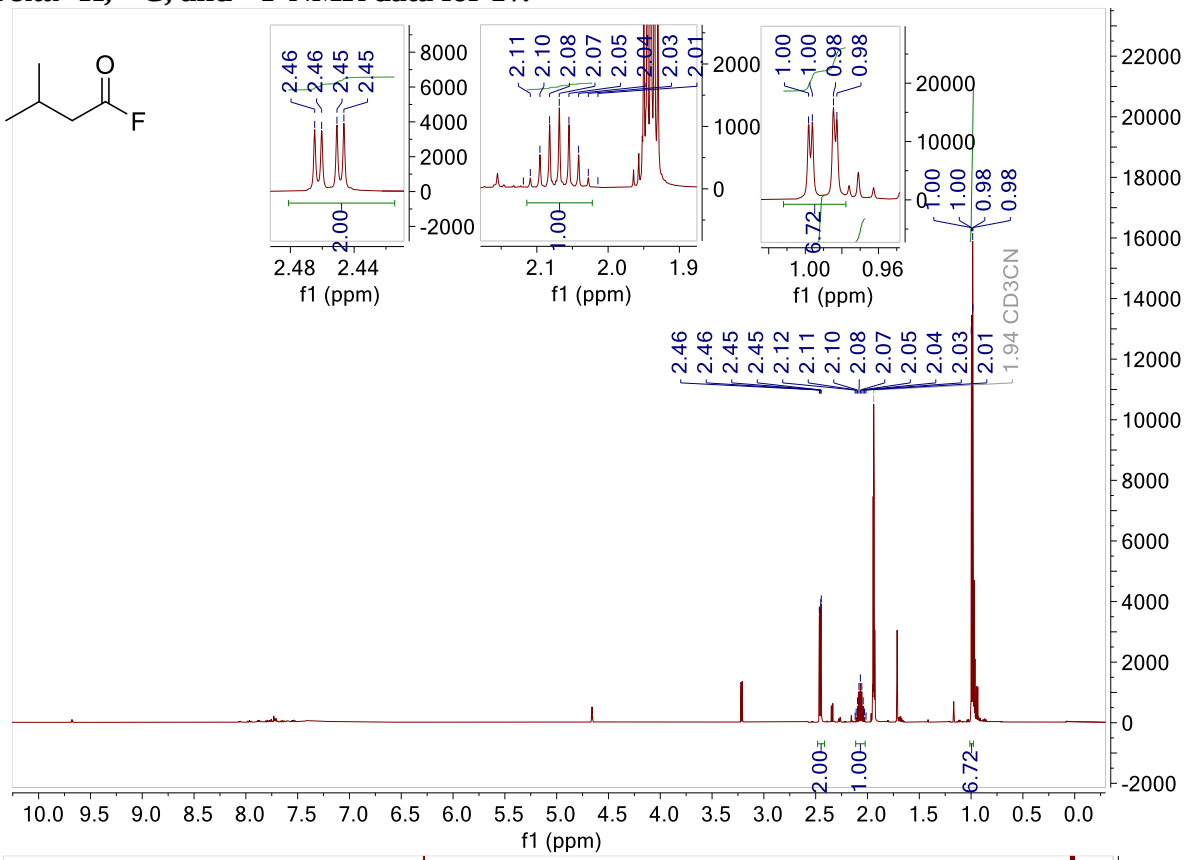


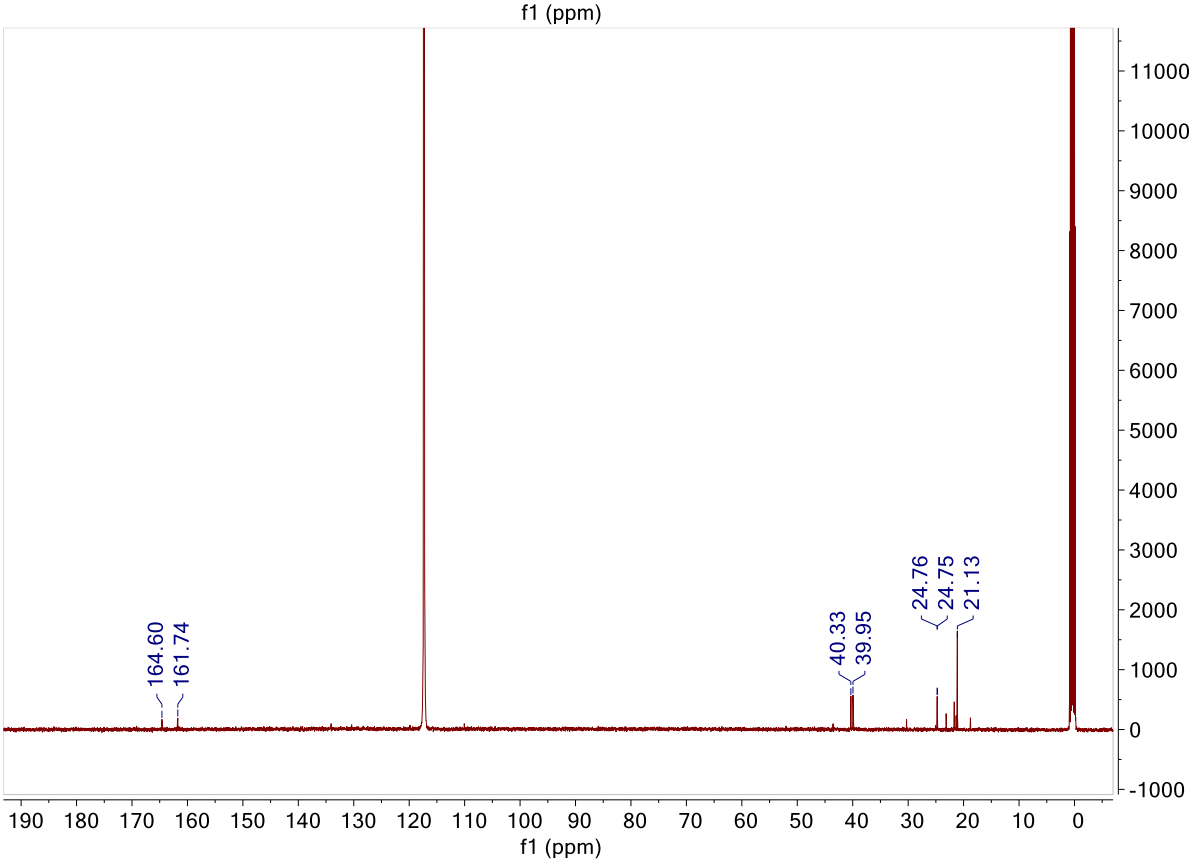

42.92
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
110
90
70
50
30
10
-10
-30
-50
-70
-90
-110
f1 (ppm)

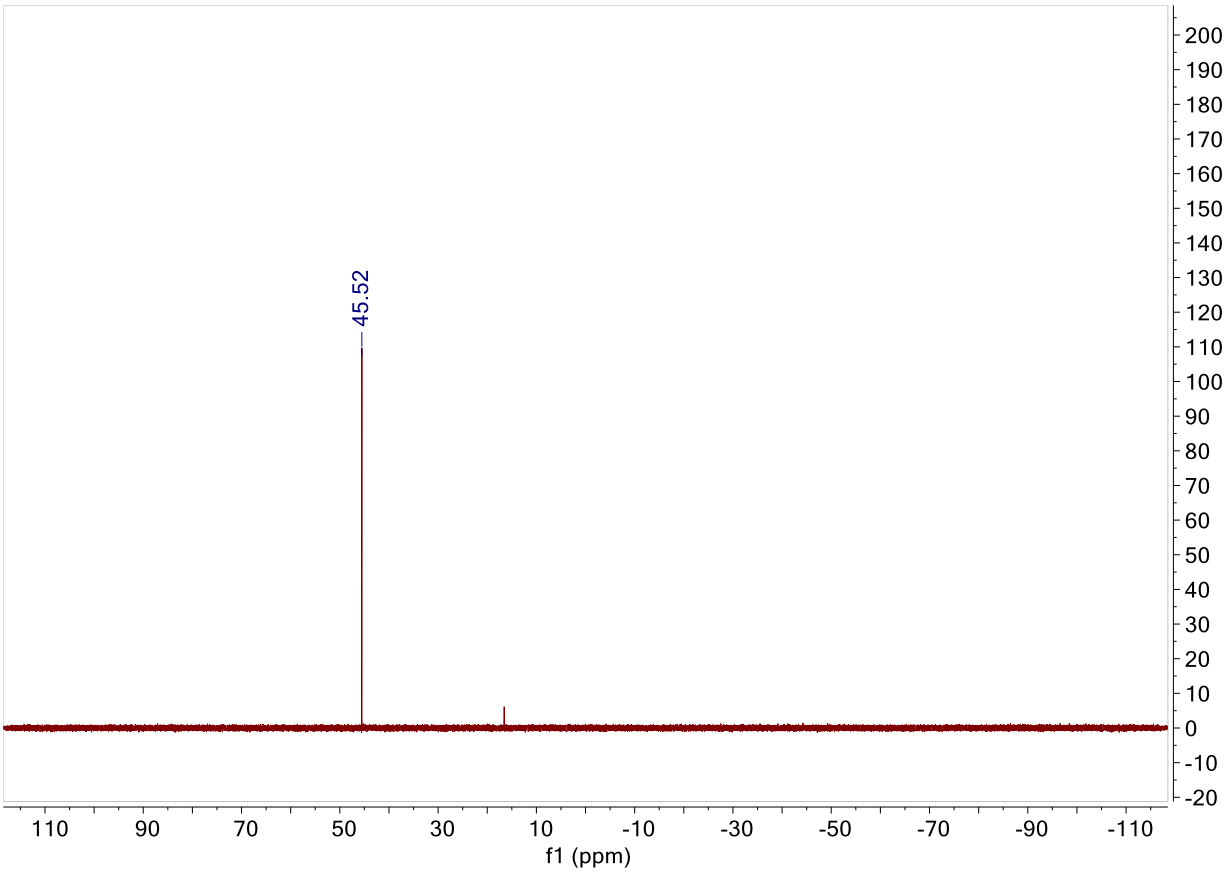
^{1}H and ^{13}C NMR data for 5u.



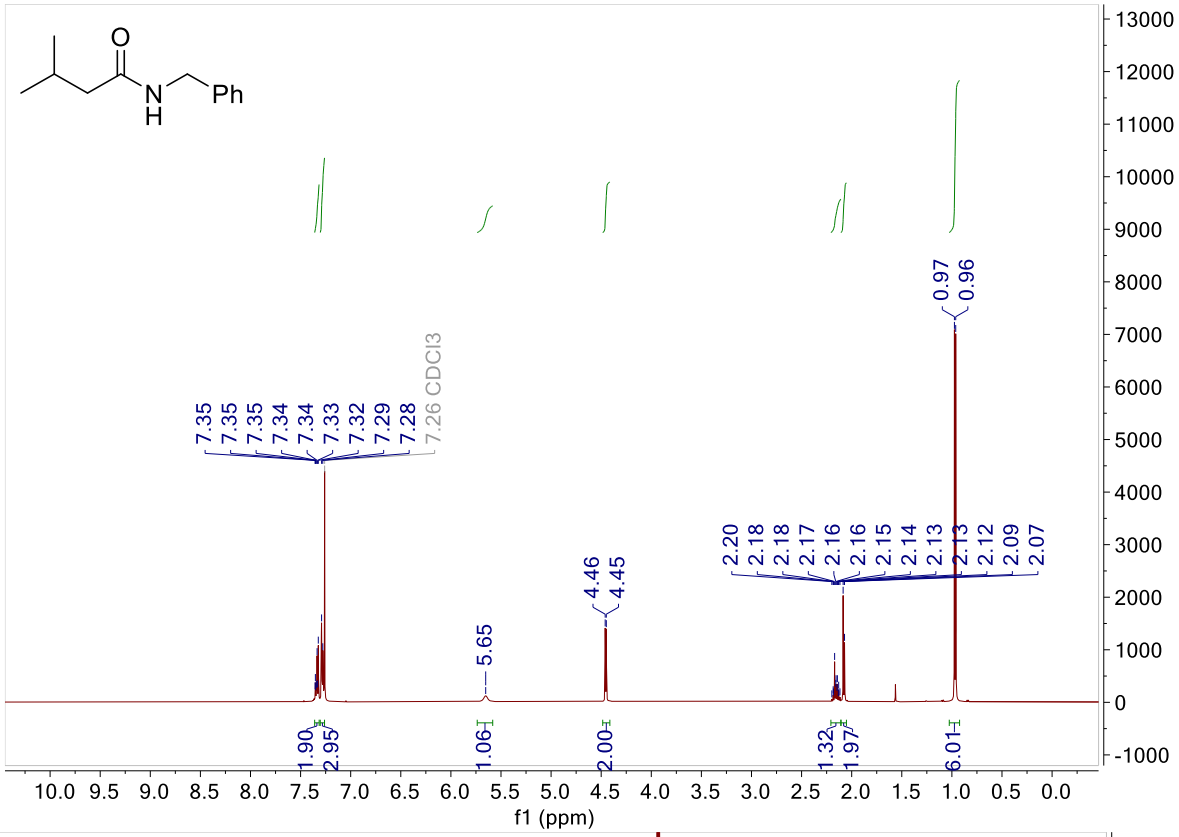
***In situ* ^{1}H, ^{13}C, and ^{19}F NMR data for 1v.**

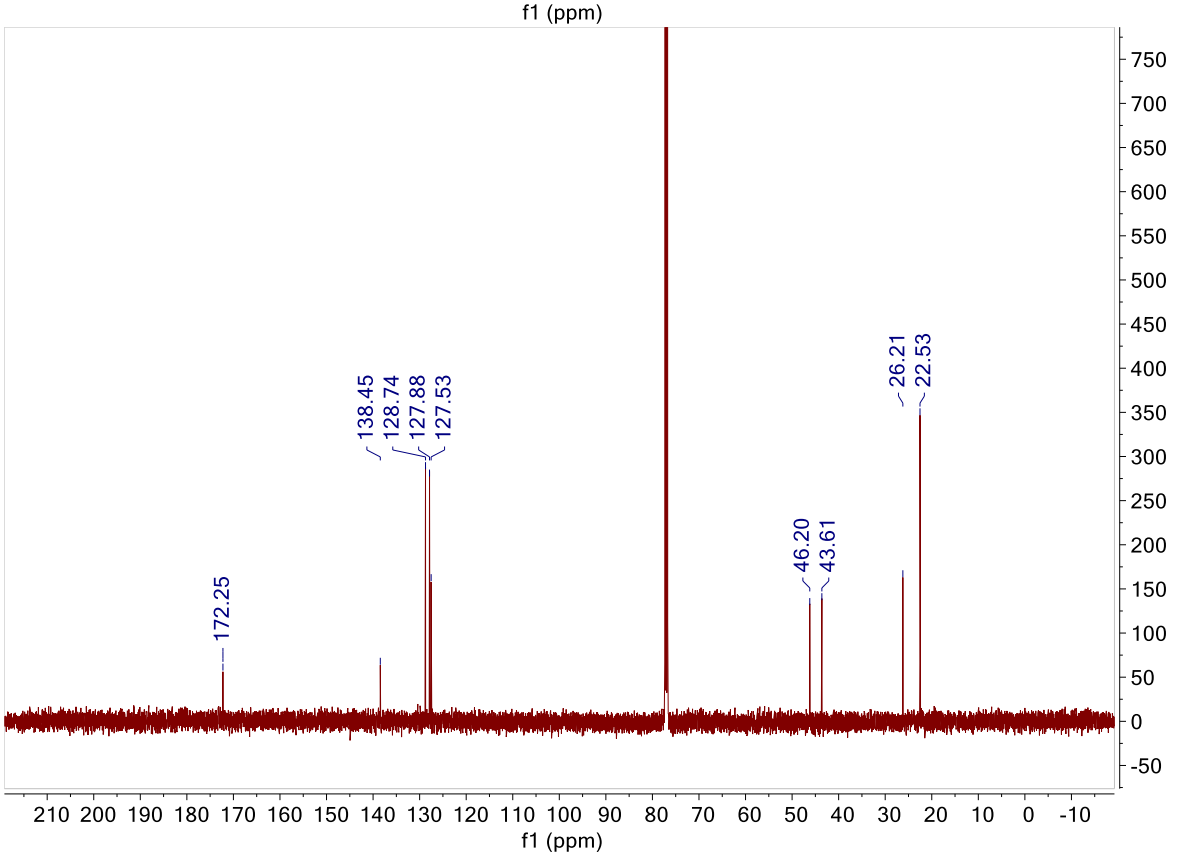




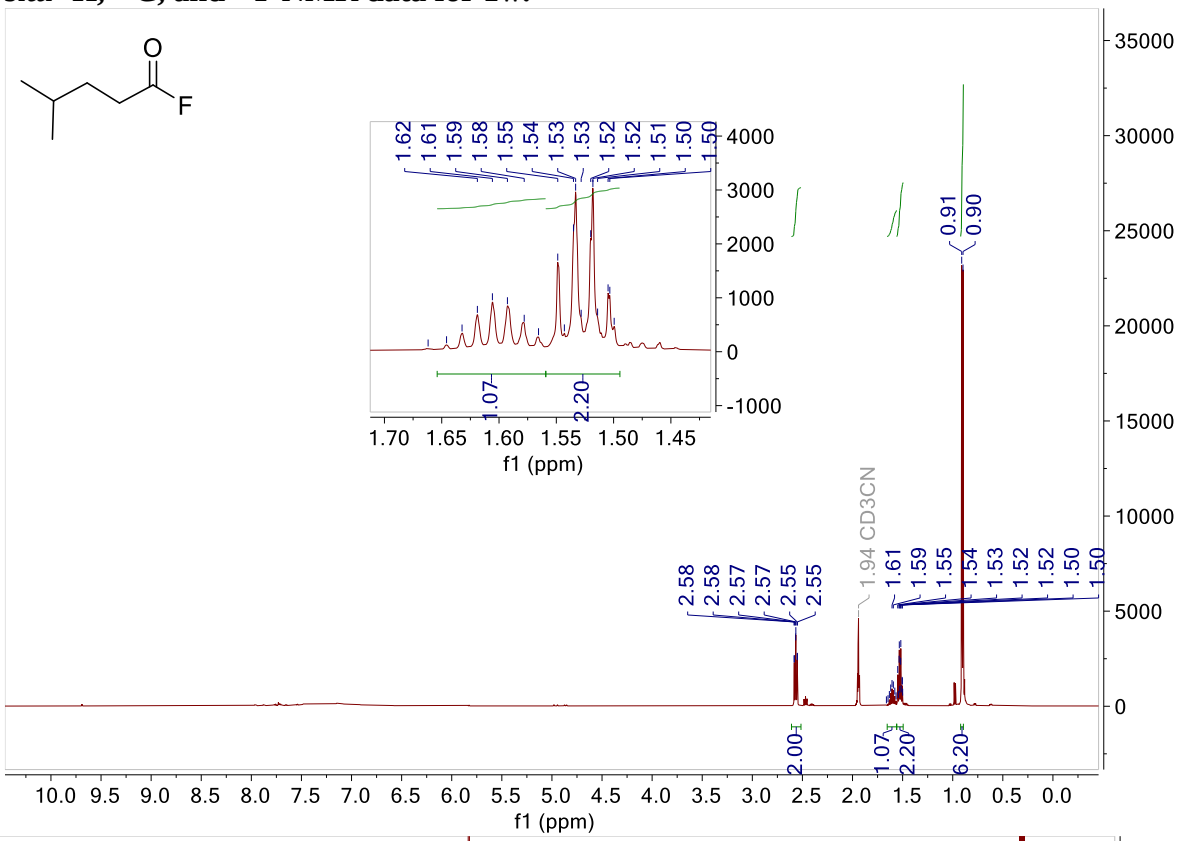

45.52
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
110
90
70
50
30
10
-10
-30
-50
-70
-90
-110
f1 (ppm)

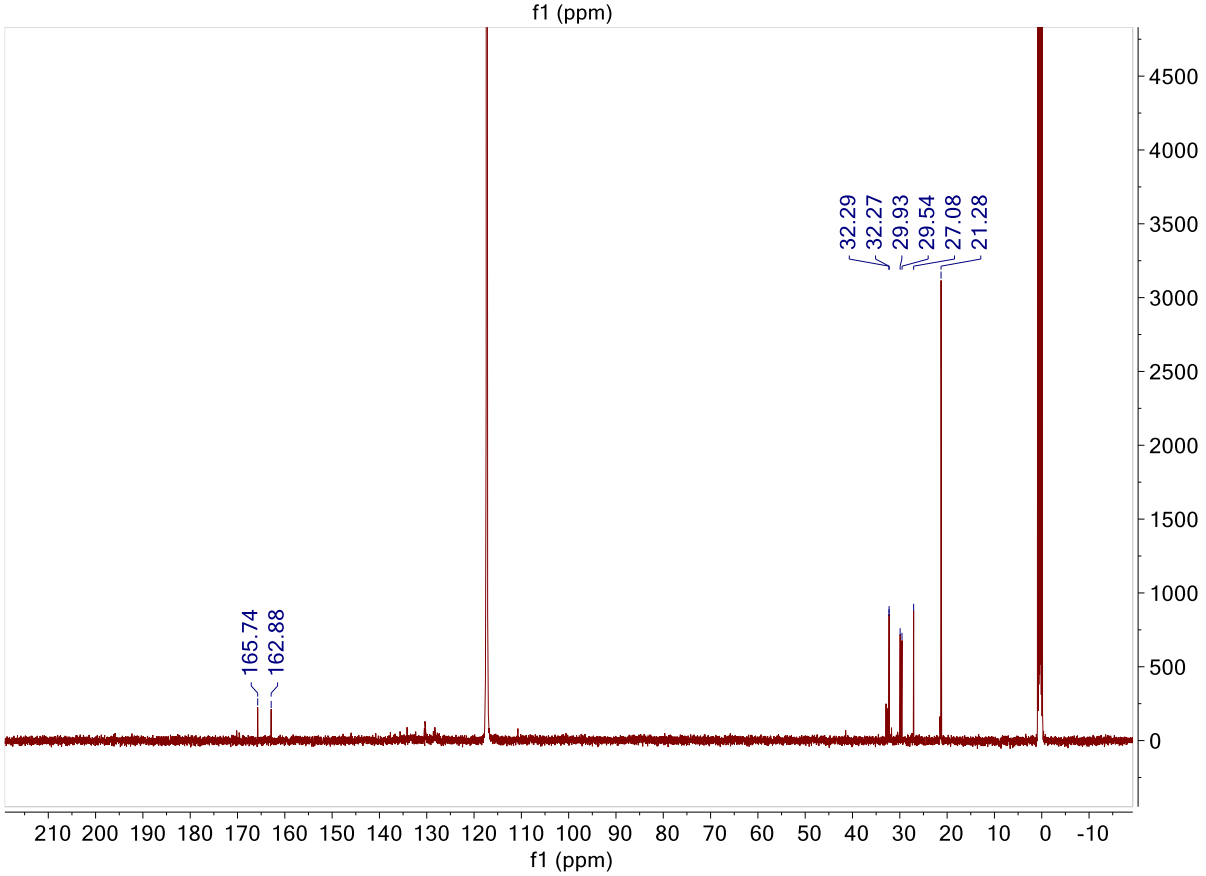
^{1}H and ^{13}C NMR data for 5v.

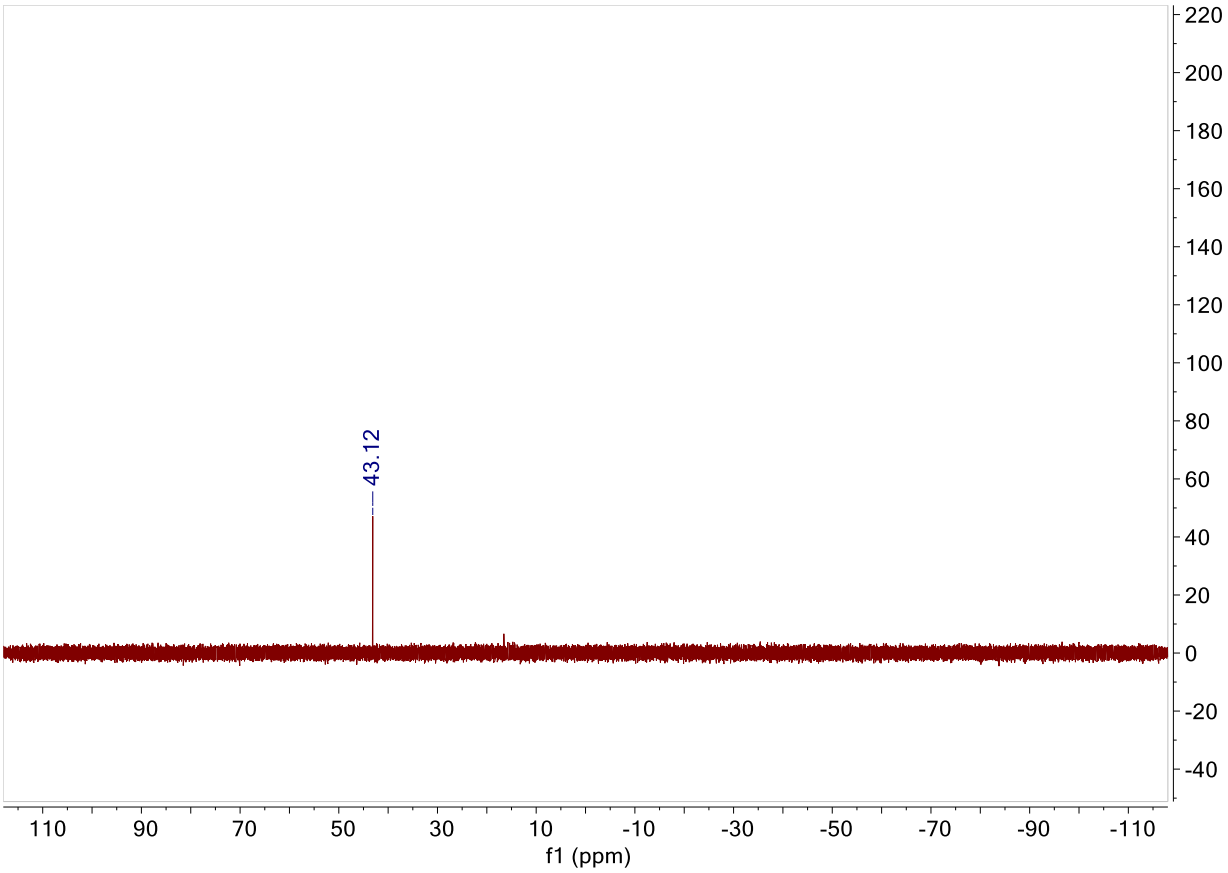




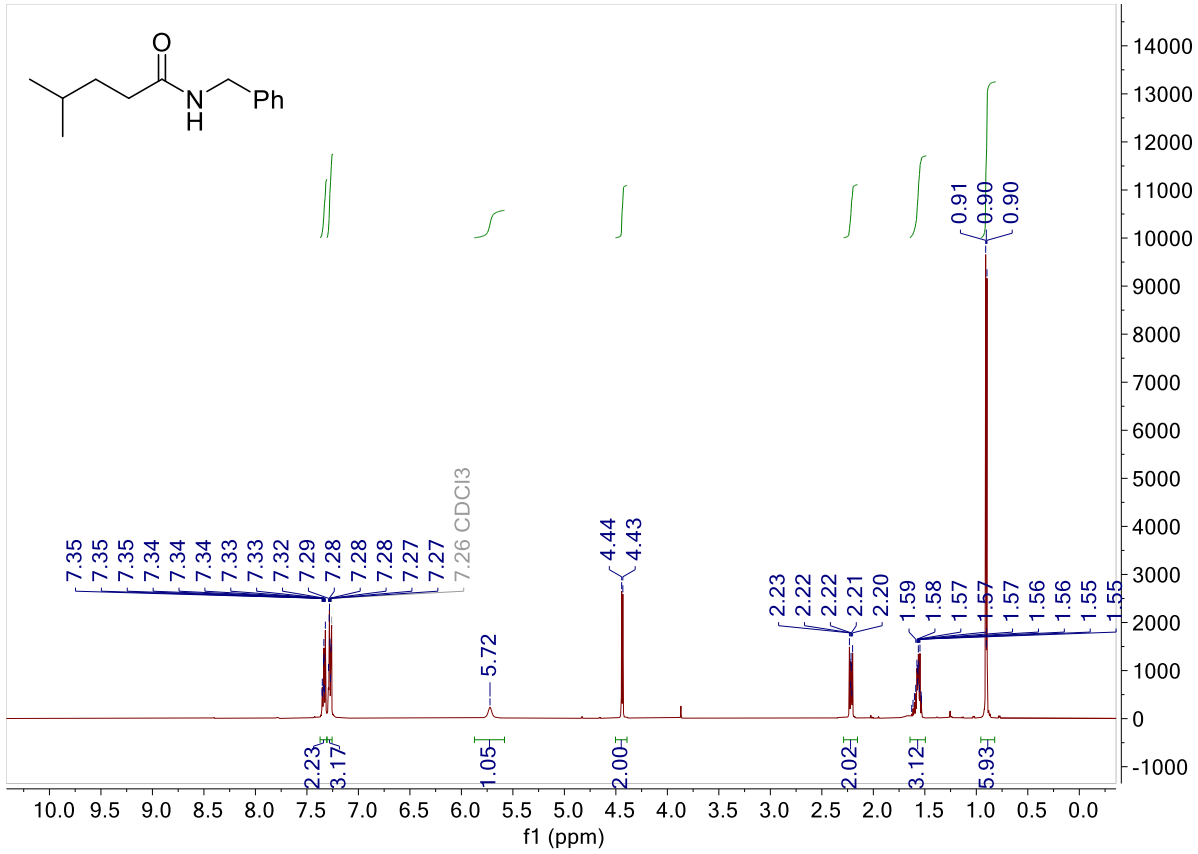
***In situ* ^{1}H, ^{13}C, and ^{19}F NMR data for 1w.**

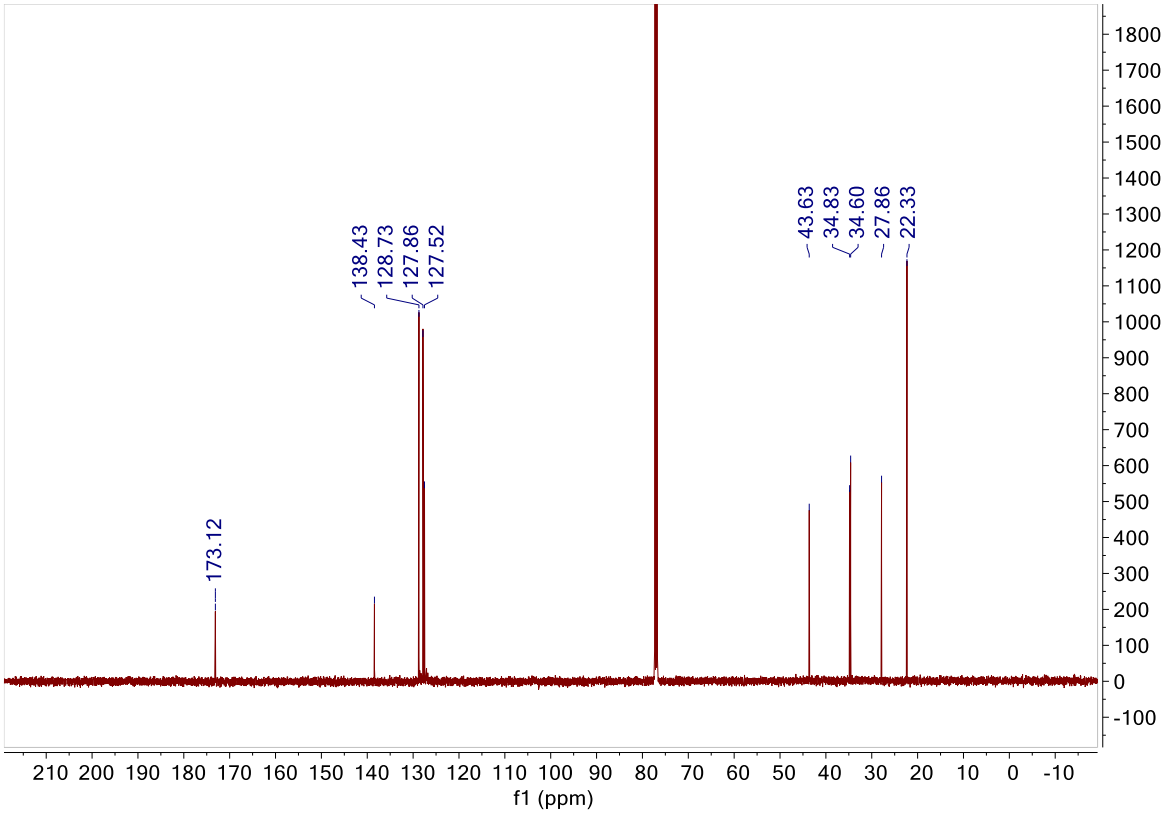




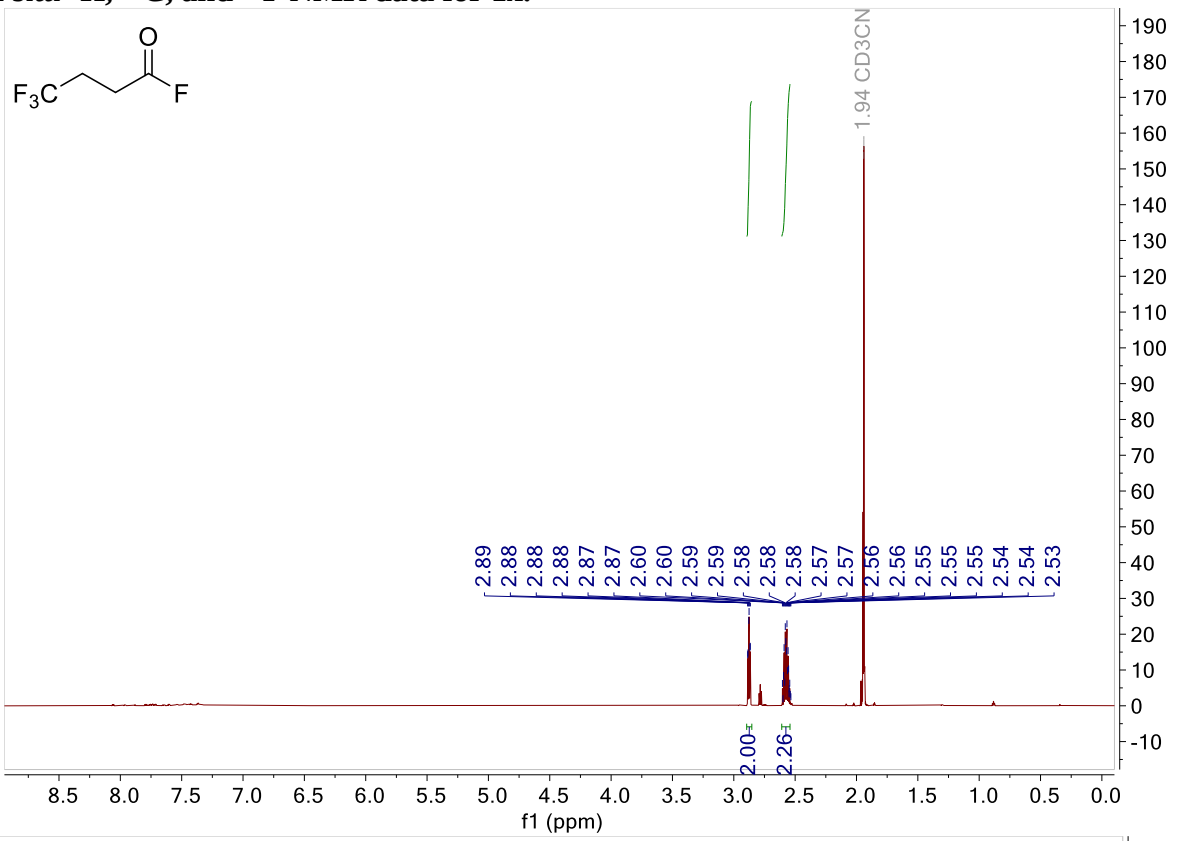

43.12
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
110
90
70
50
30
10
-10
-30
-50
-70
-90
-110
f1 (ppm)

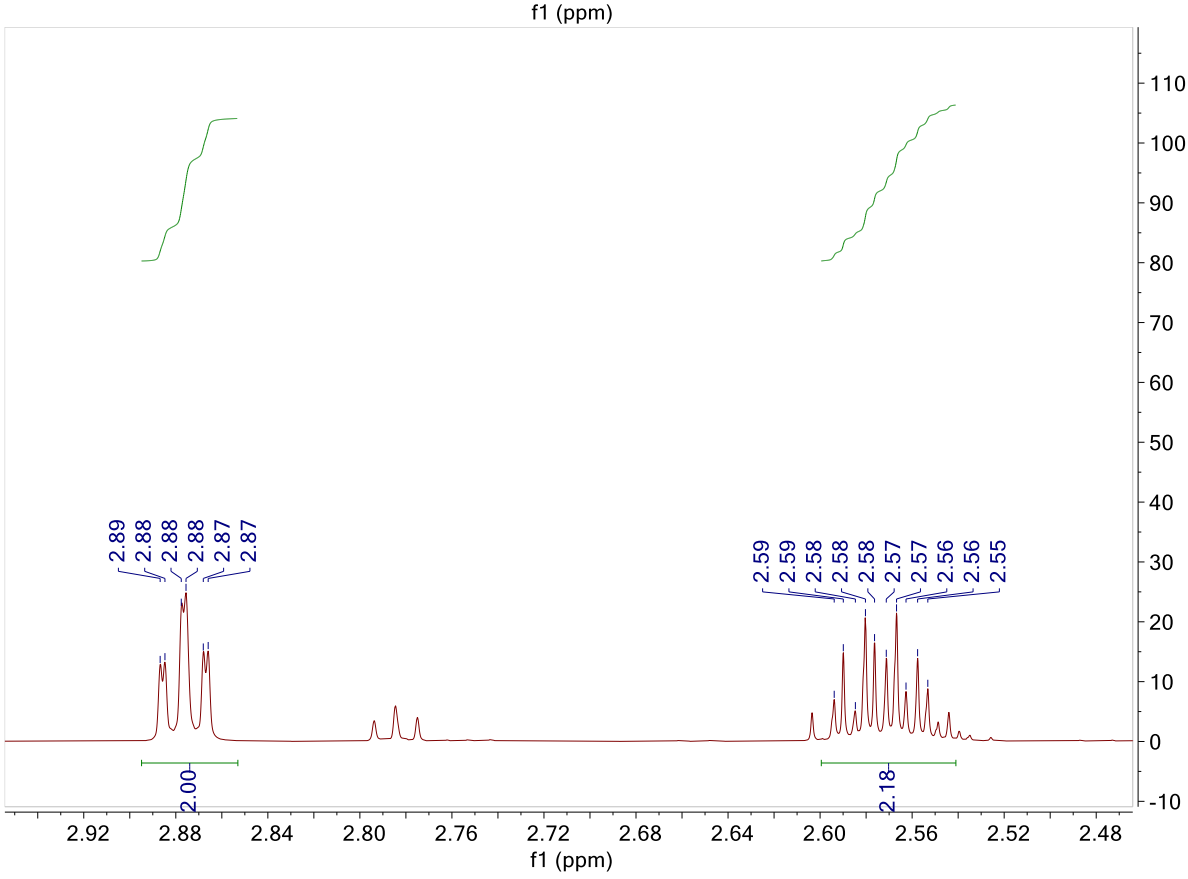
^{1}H and ^{13}C NMR data for 5w.

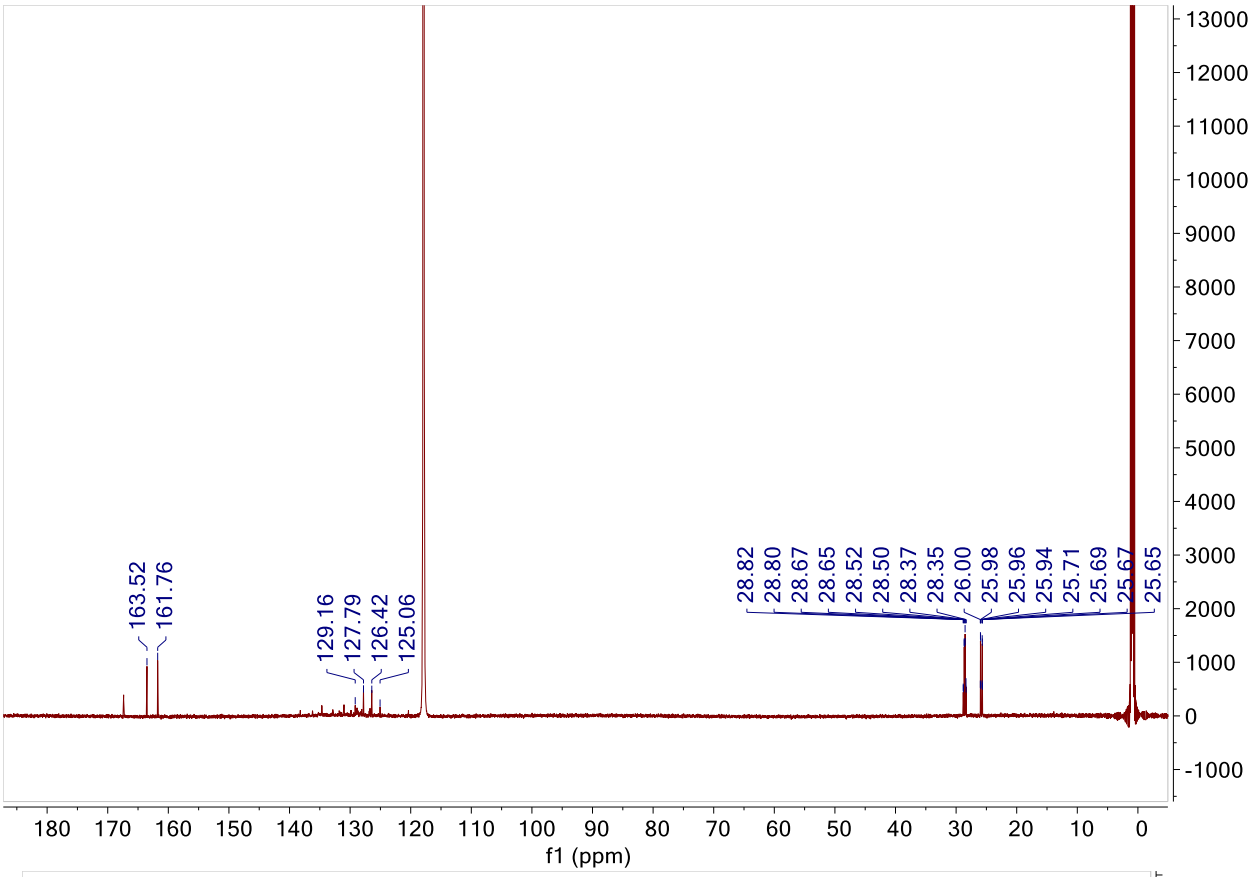


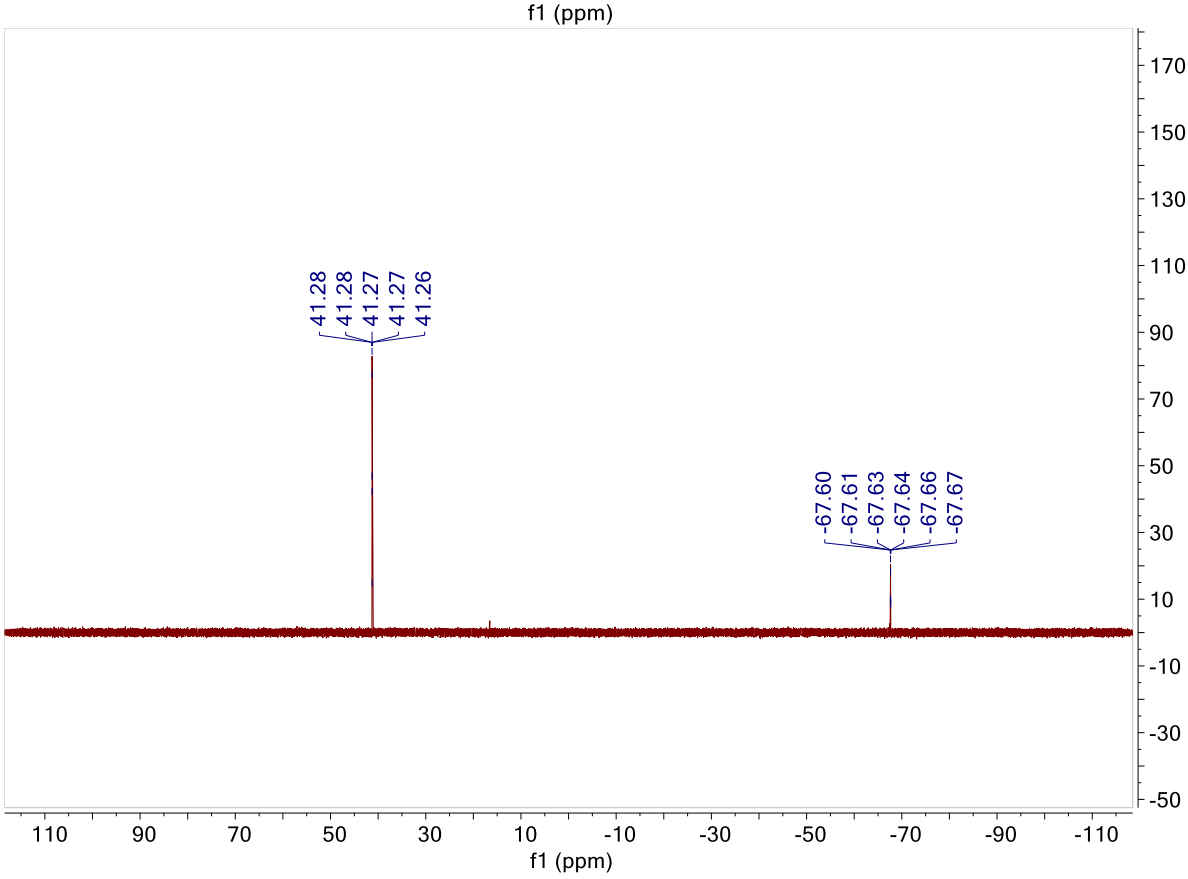


***In situ* ^{1}H, ^{13}C, and ^{19}F NMR data for 1x.**

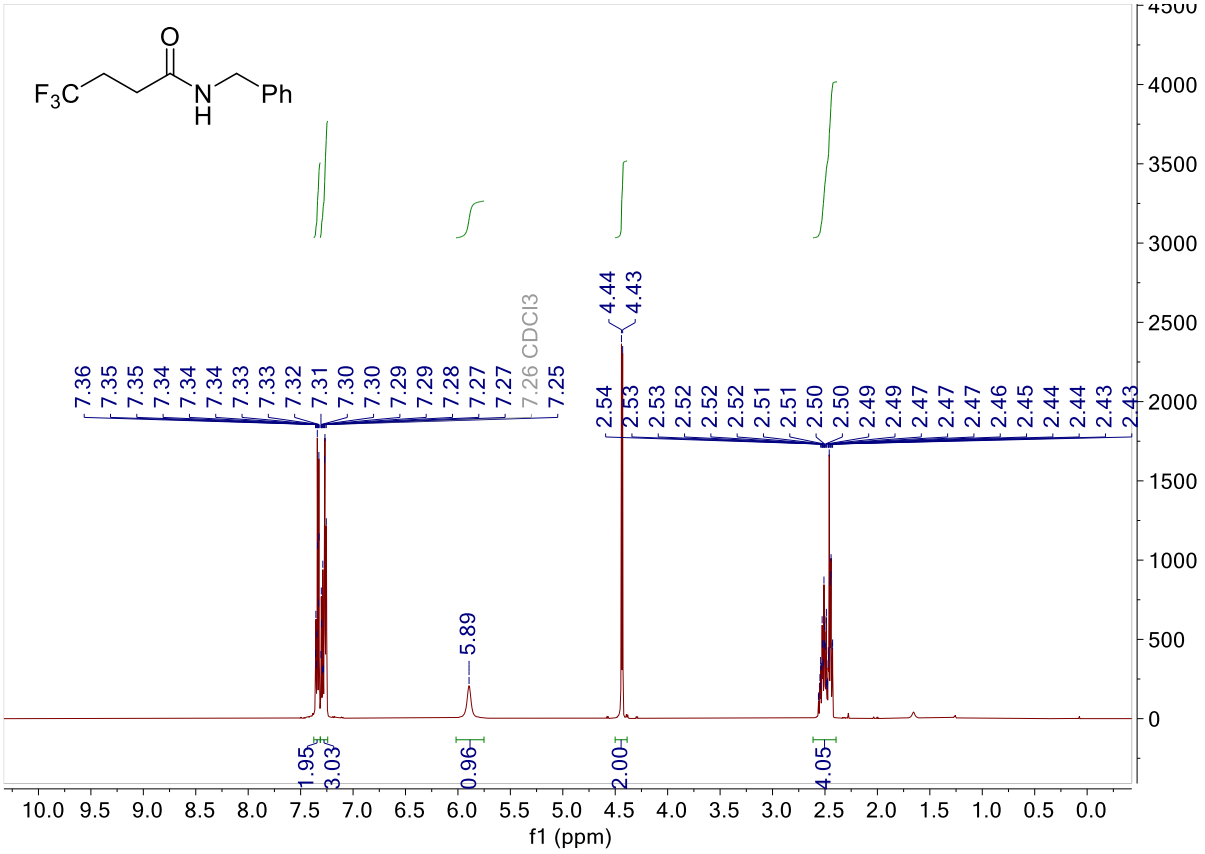


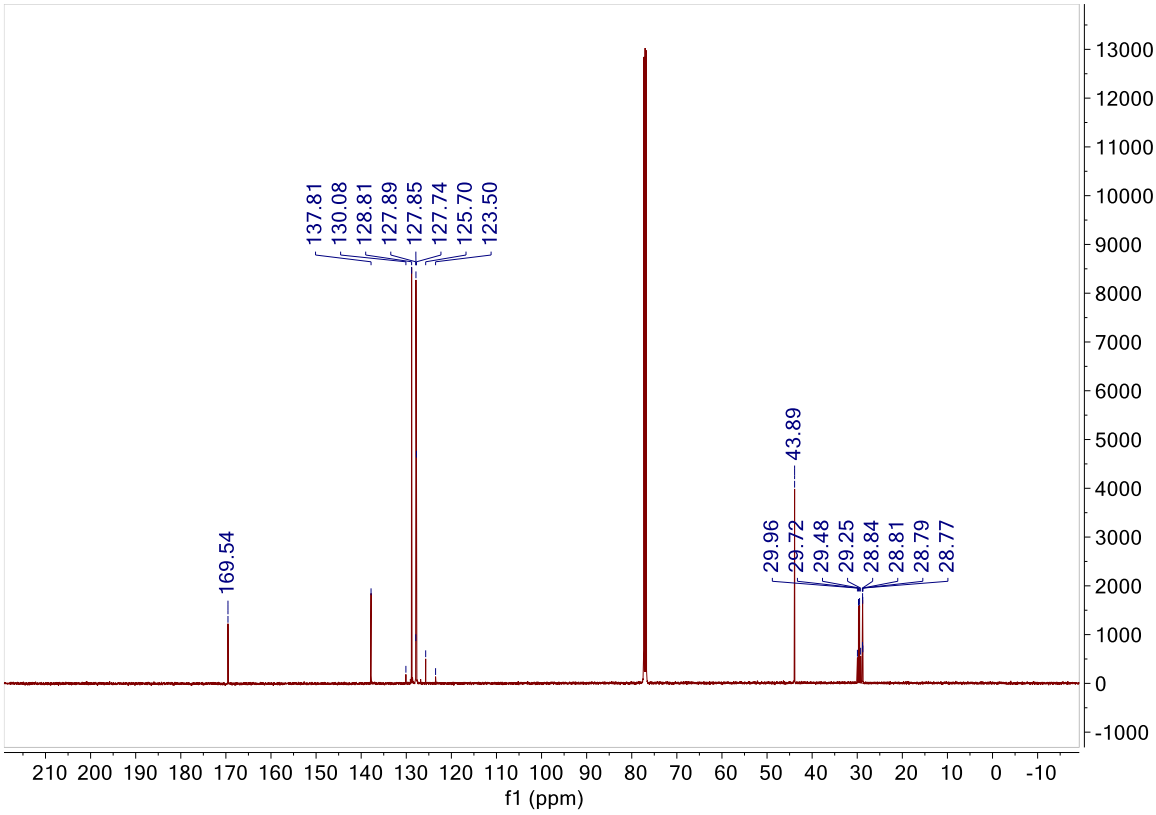



163.52
161.76
129.16
127.79
126.42
125.06
28.82
28.80
28.67
28.65
28.52
28.50
28.37
28.35
26.00
25.98
25.96
25.94
25.71
25.69
25.67
25.65
f1 (ppm)

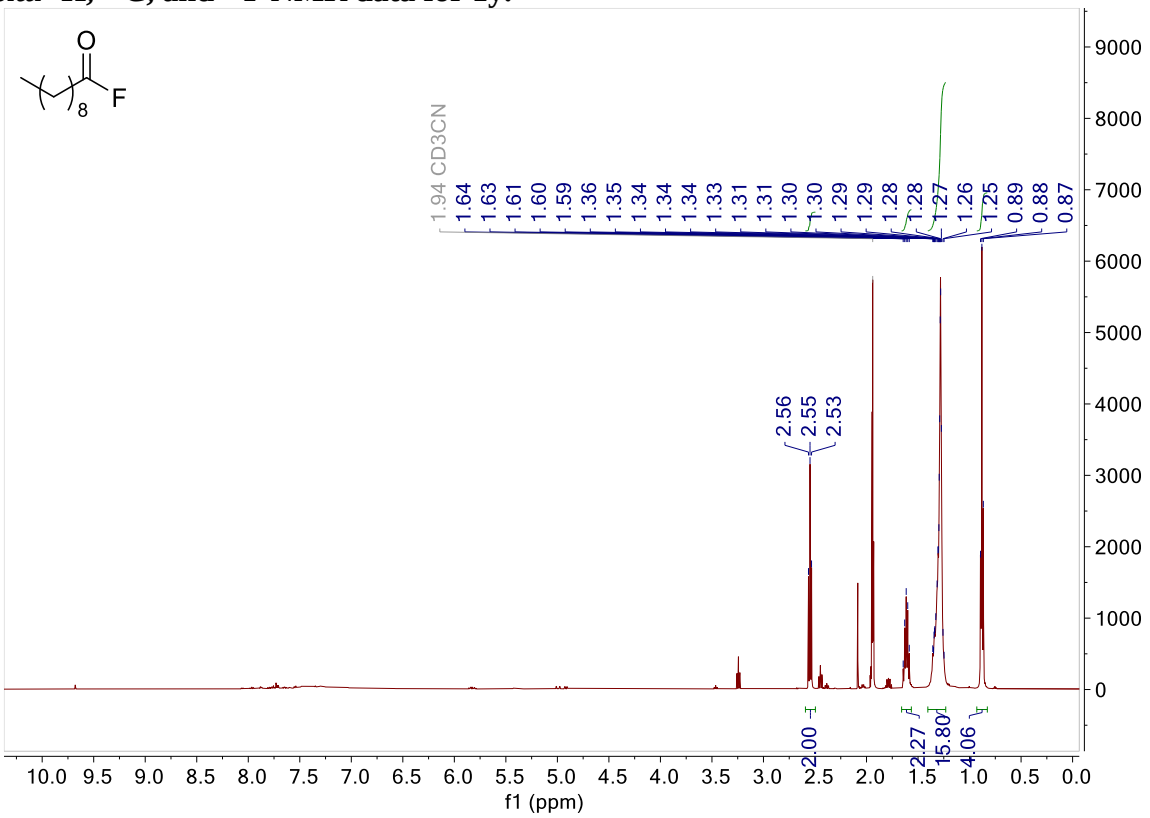

41.28
41.28
41.27
41.27
41.26
-67.60
-67.61
-67.63
-67.64
-67.66
-67.67
f1 (ppm)

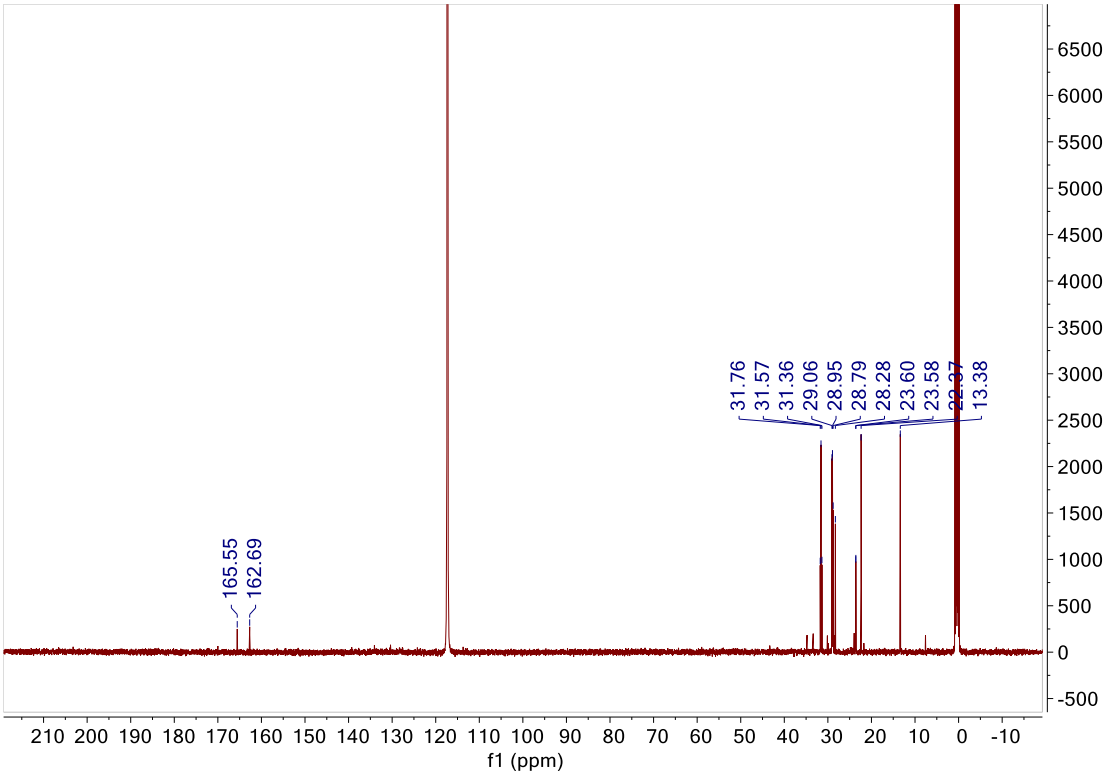
^{1}H and ^{13}C NMR data for 5x.

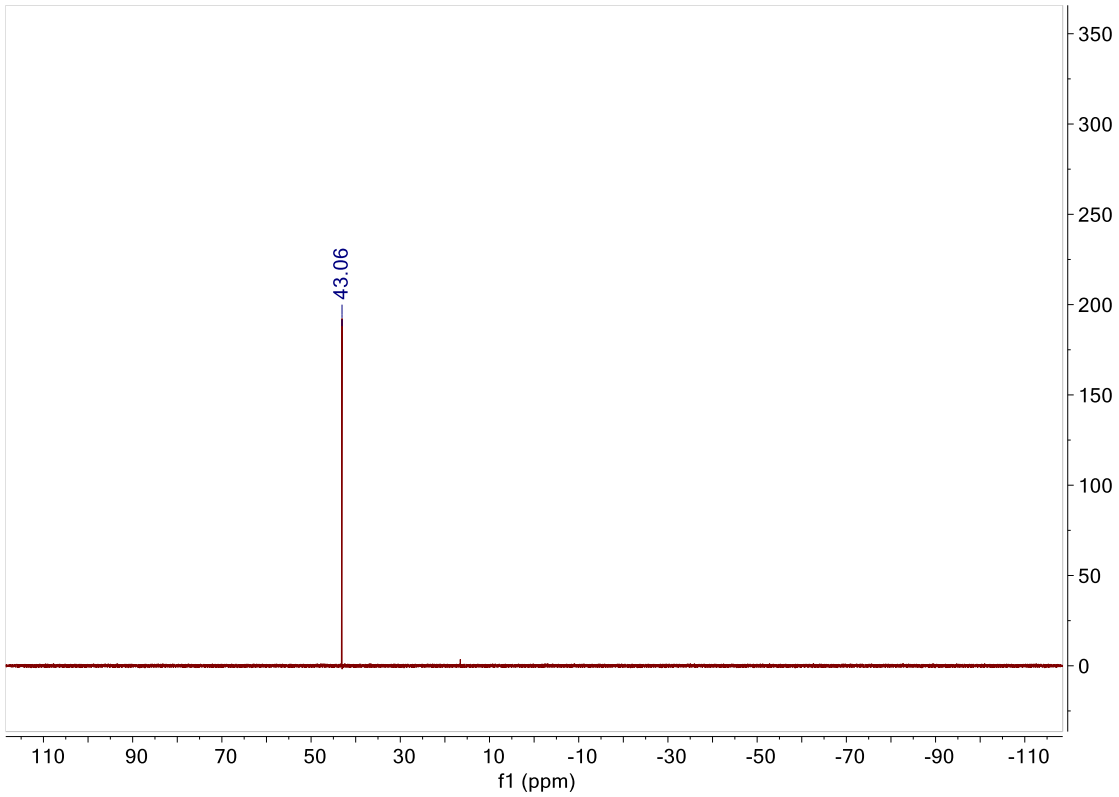




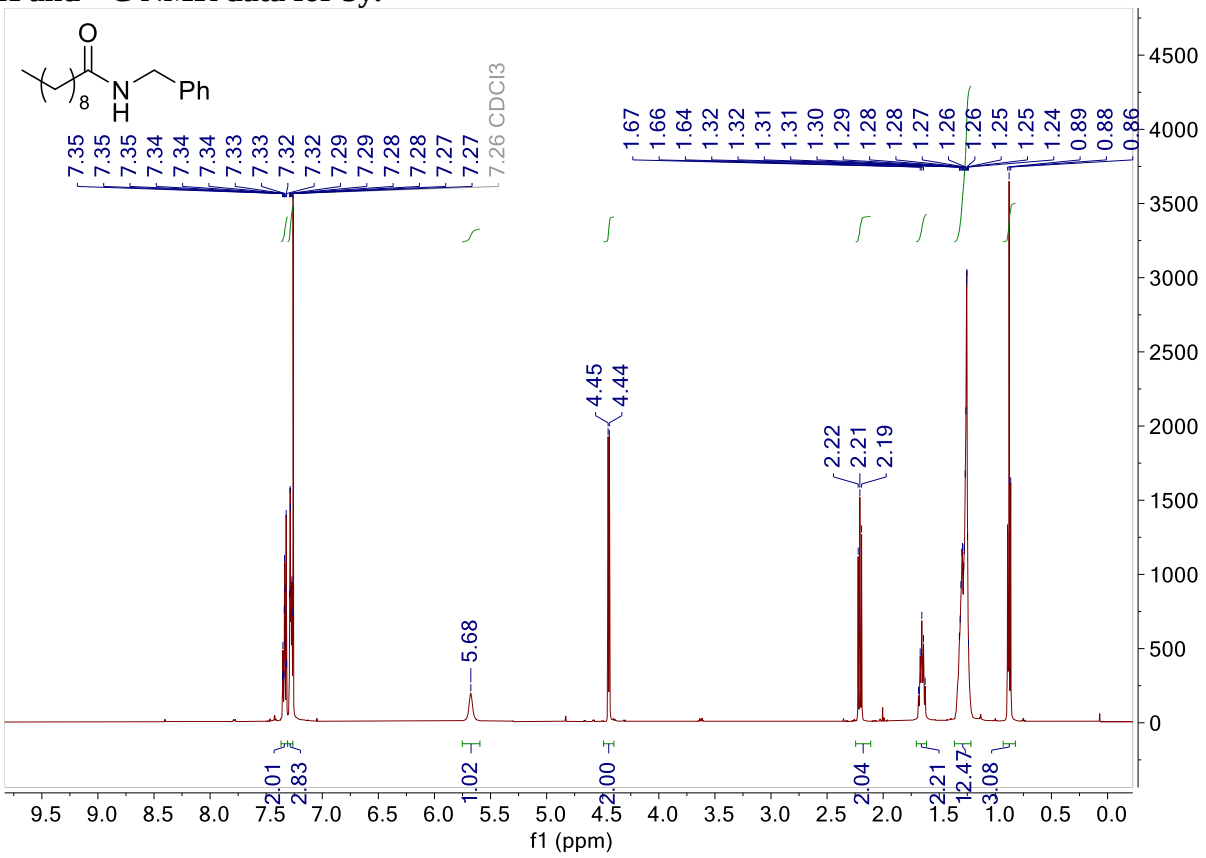
***In situ* ^{1}H, ^{13}C, and ^{19}F NMR data for 1y.**

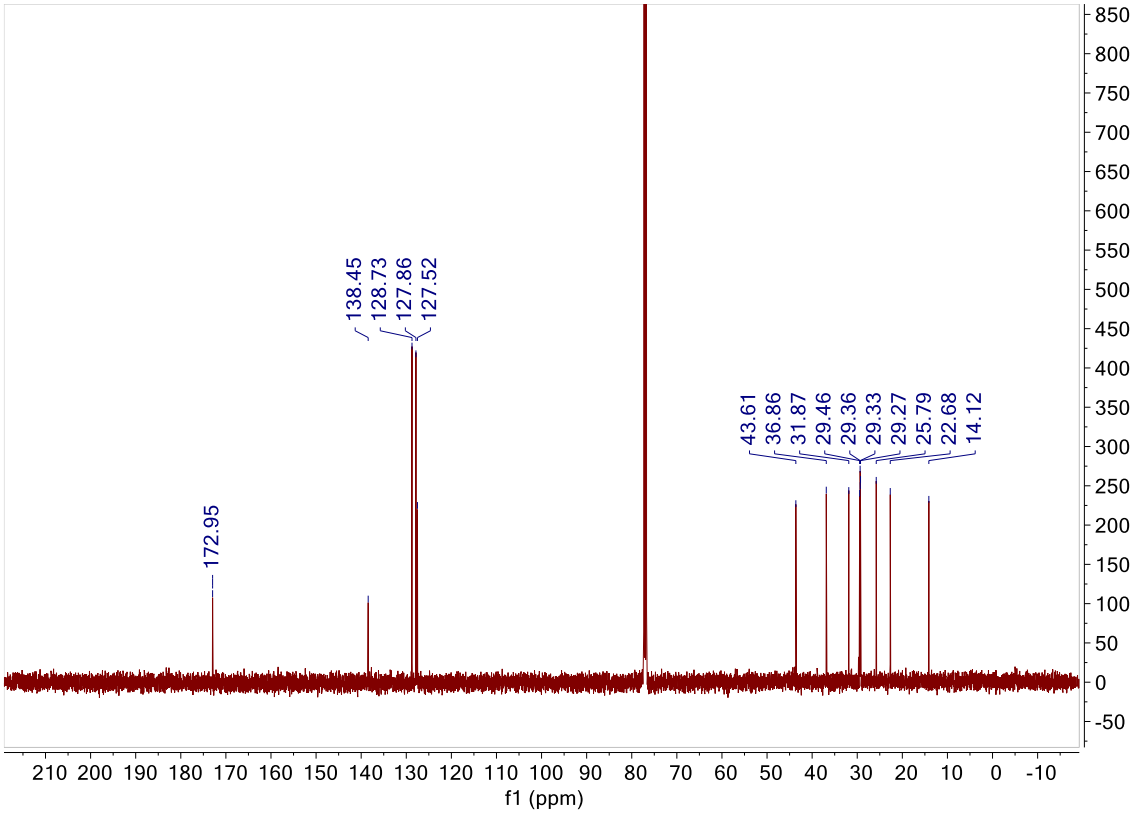




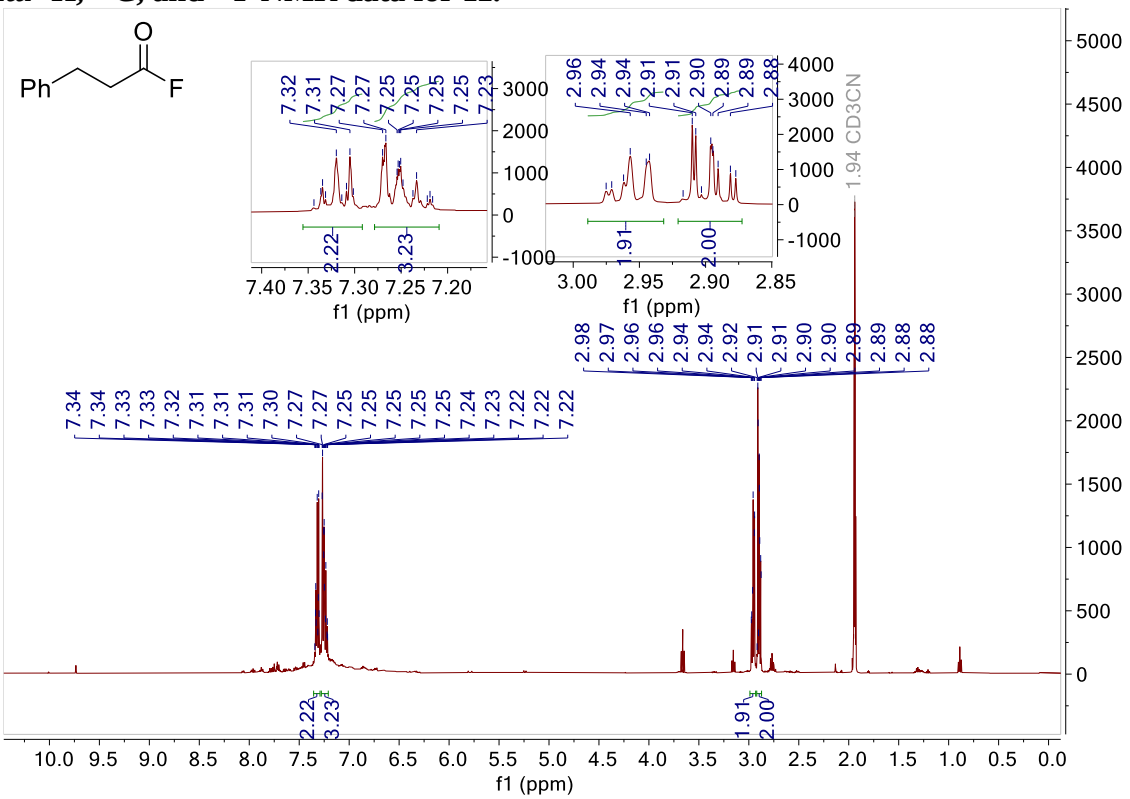

43.06
350
300
250
200
150
100
50
0
110
90
70
50
30
10
-10
-30
-50
-70
-90
-110
f1 (ppm)

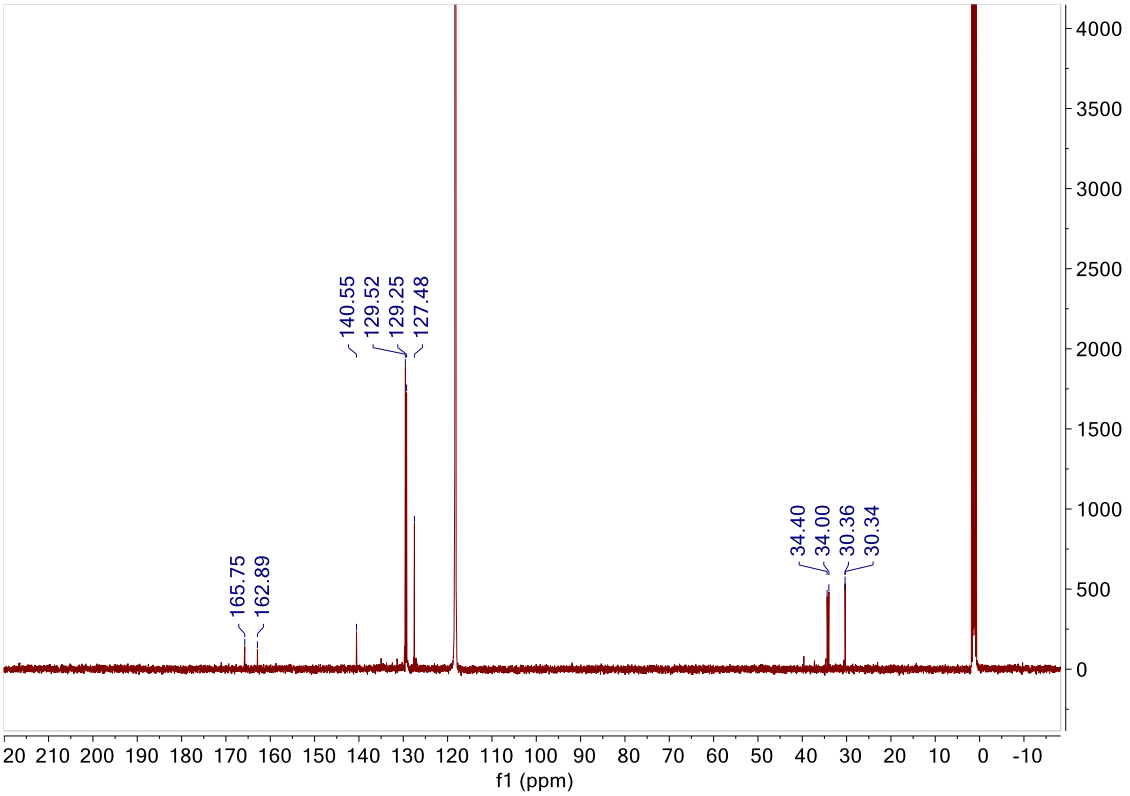
^{1}H and ^{13}C NMR data for 5y.

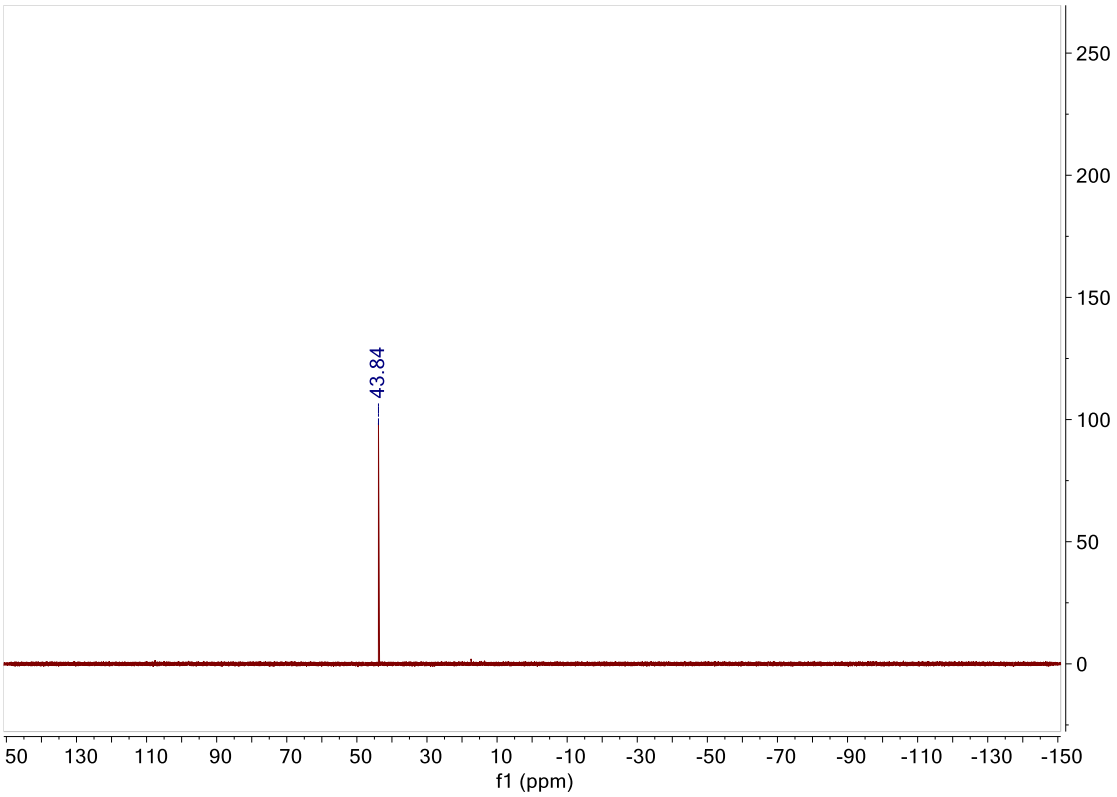




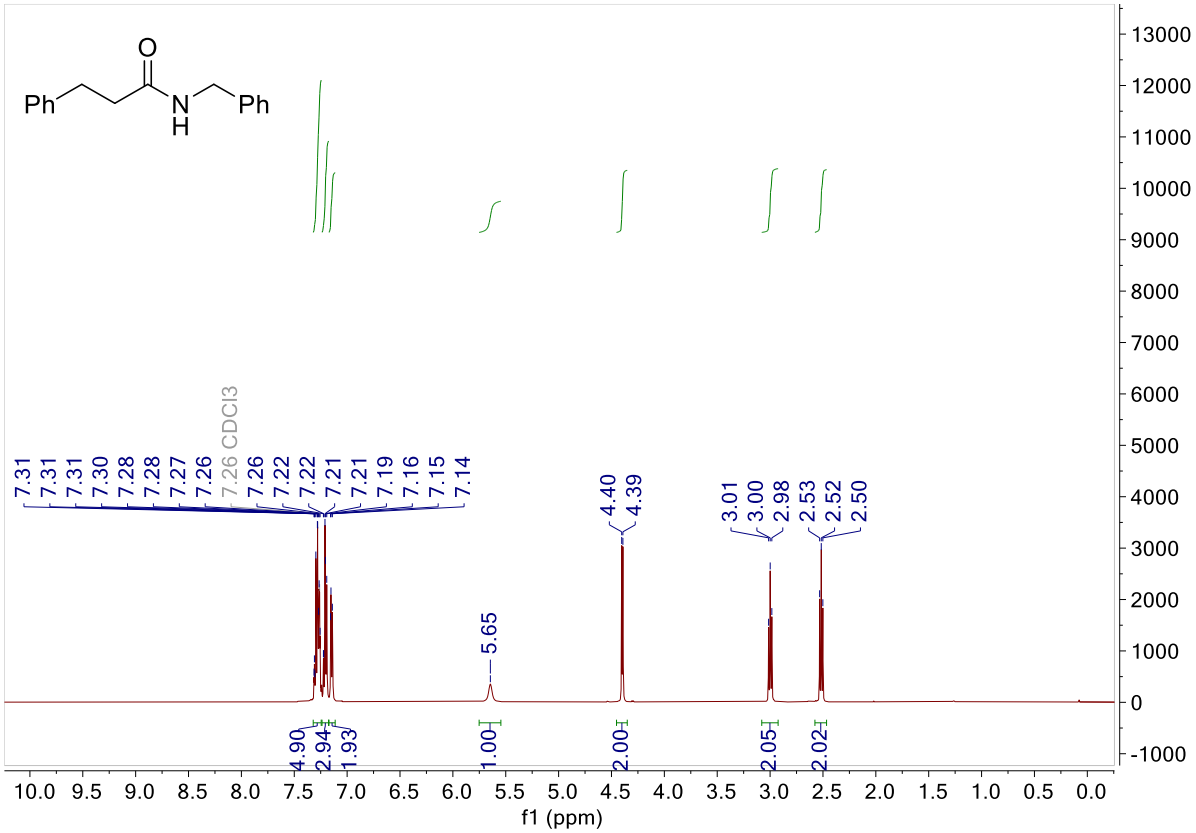
***In situ* ^{1}H, ^{13}C, and ^{19}F NMR data for 1z.**

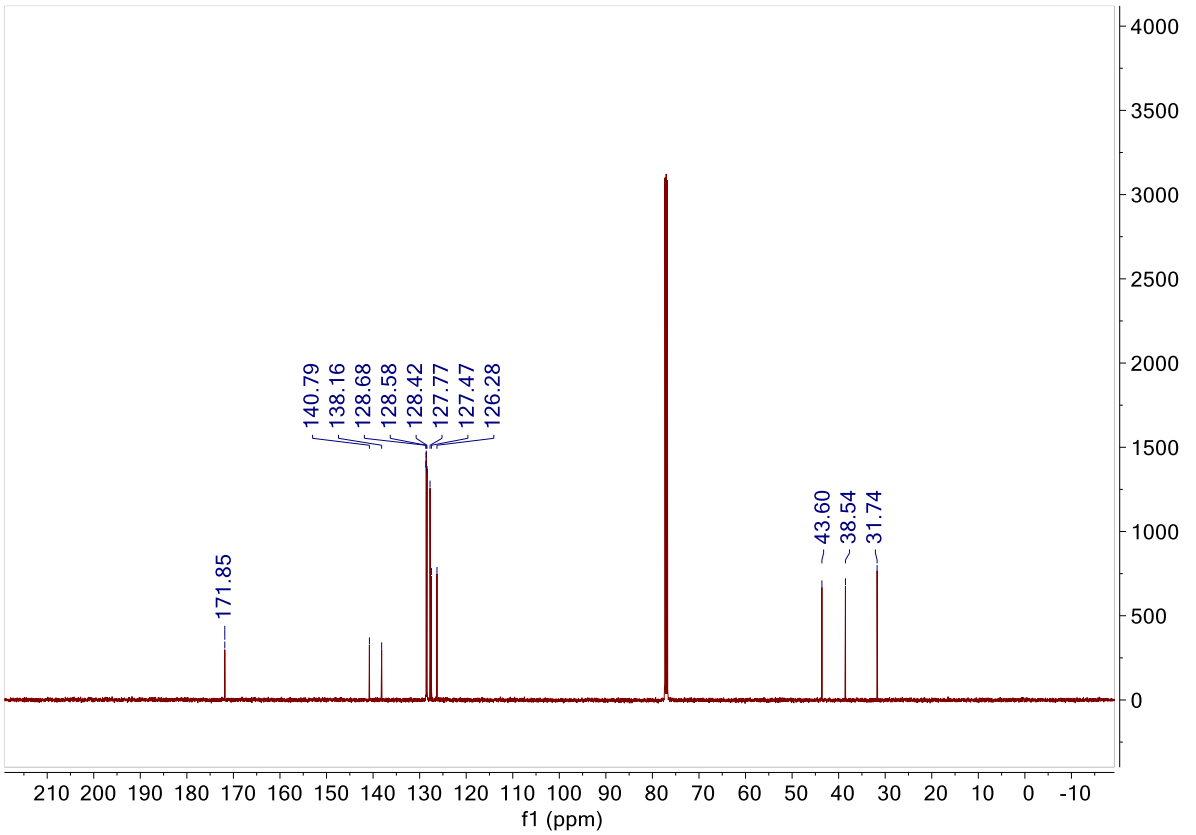




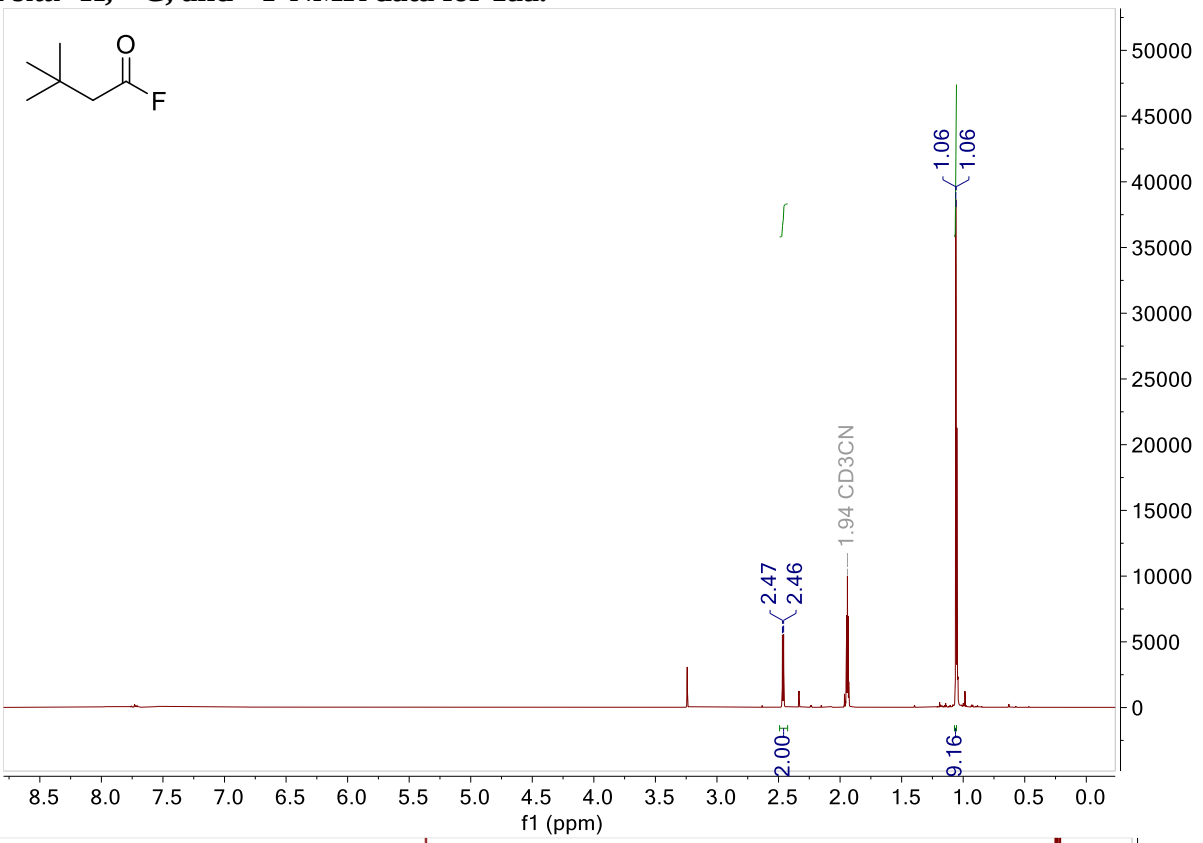

43.84
250
200
150
100
50
0
50 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150
f1 (ppm)

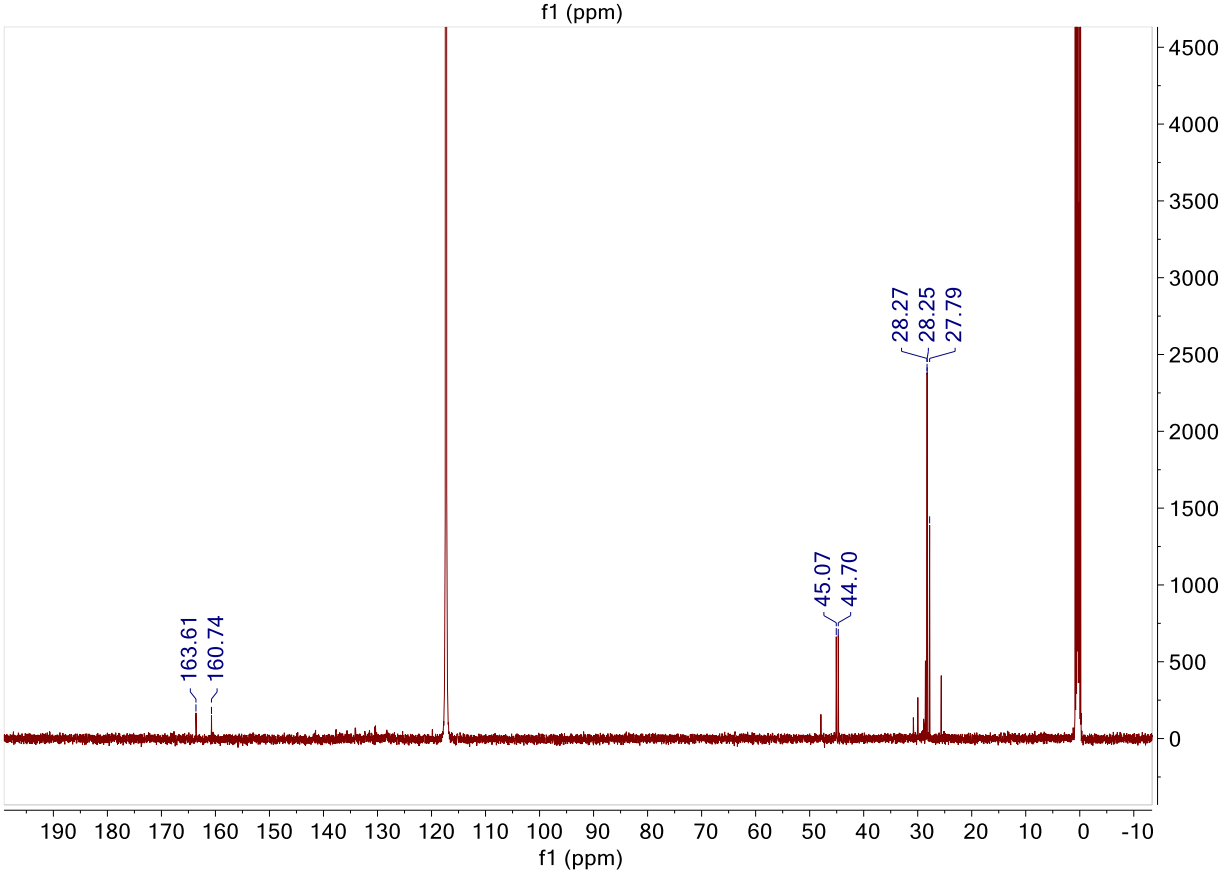
^{1}H and ^{13}C NMR data for 5z.

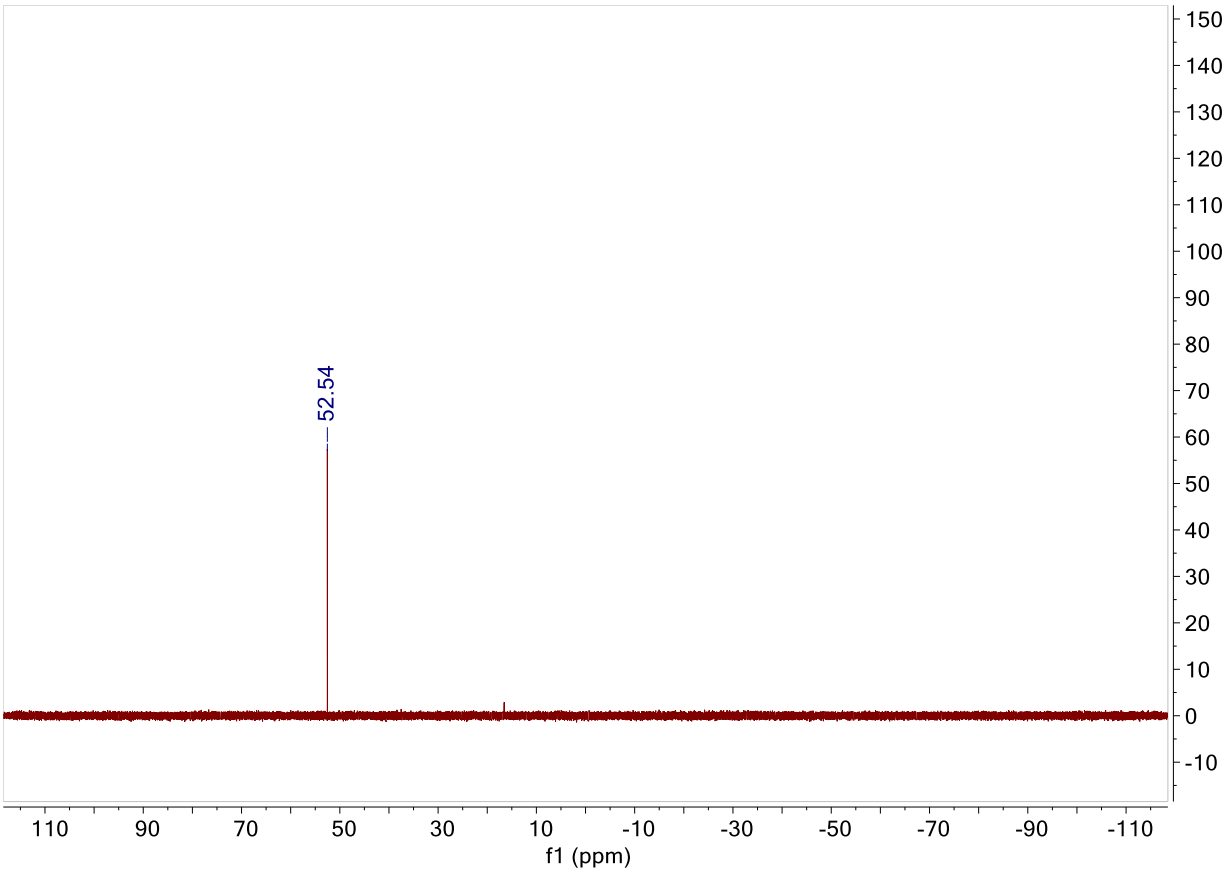




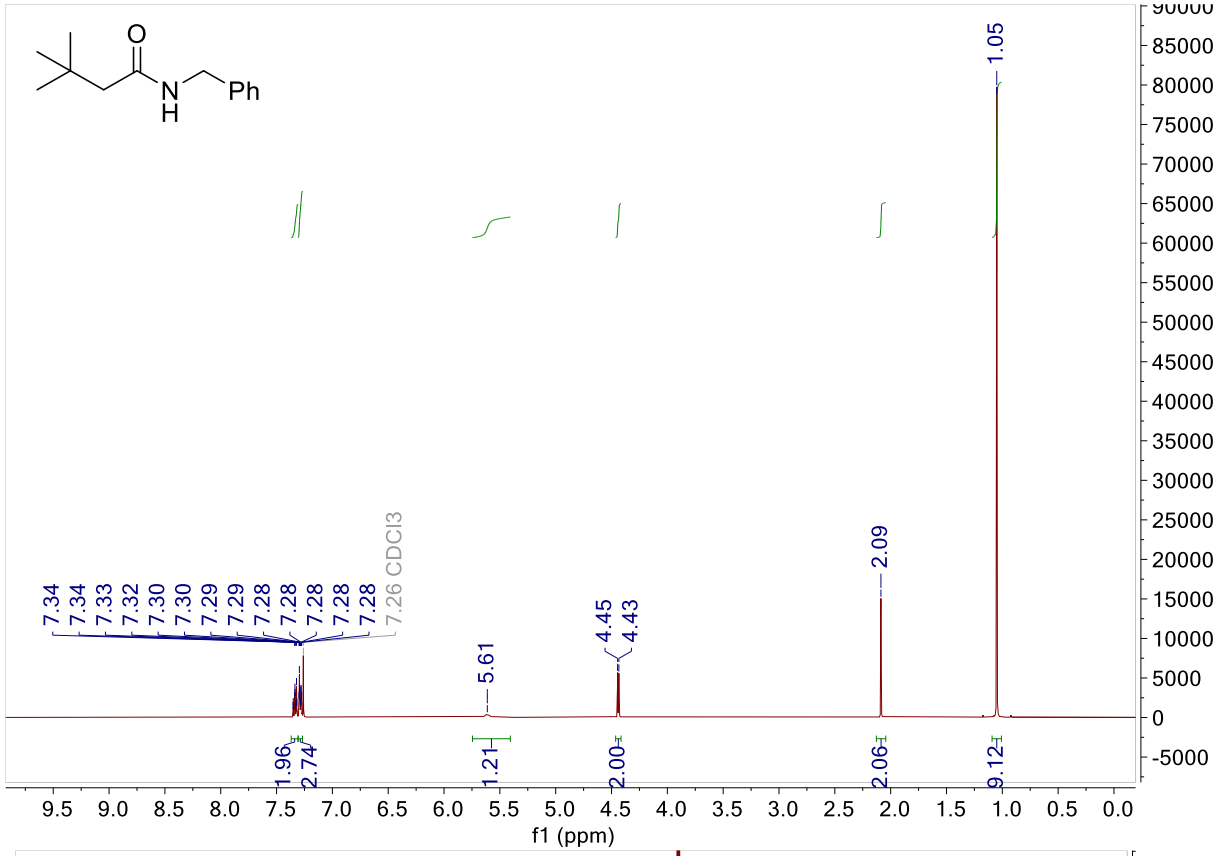
***In situ* ^{1}H, ^{13}C, and ^{19}F NMR data for 1aa.**

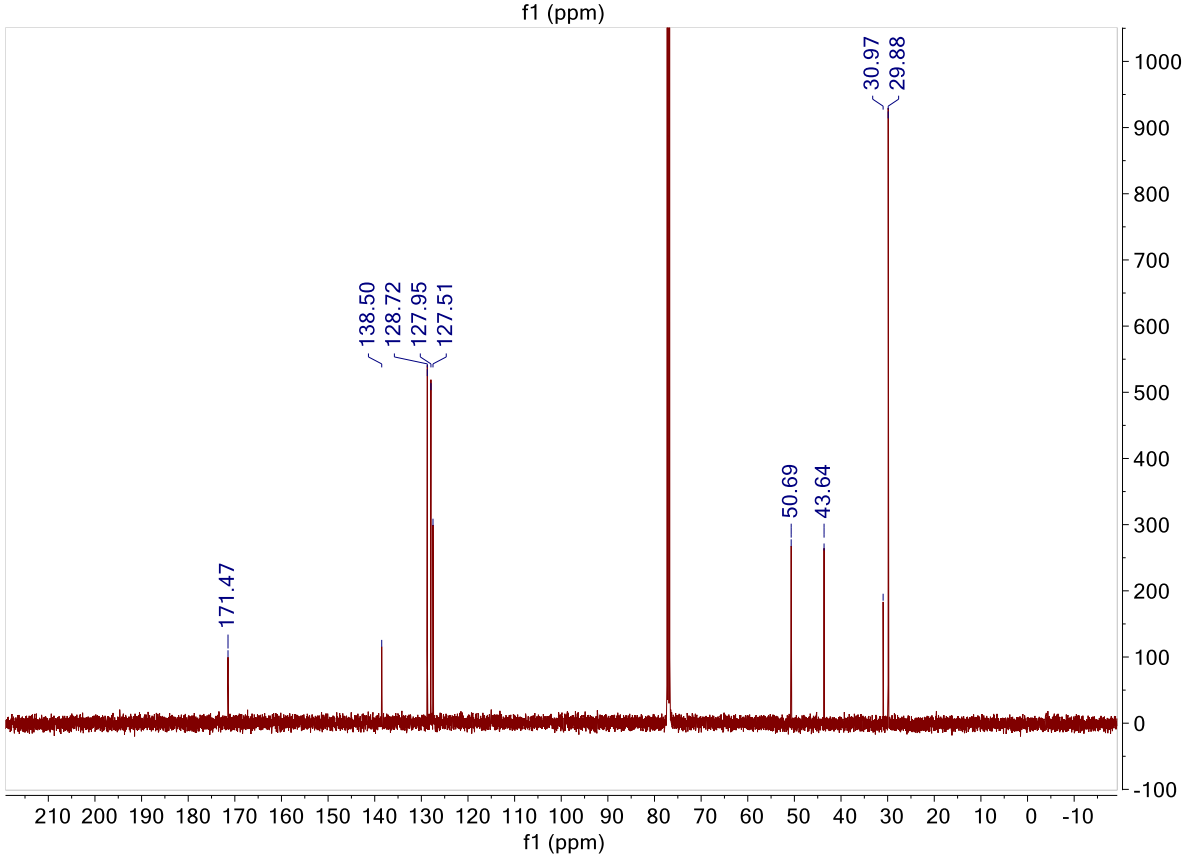




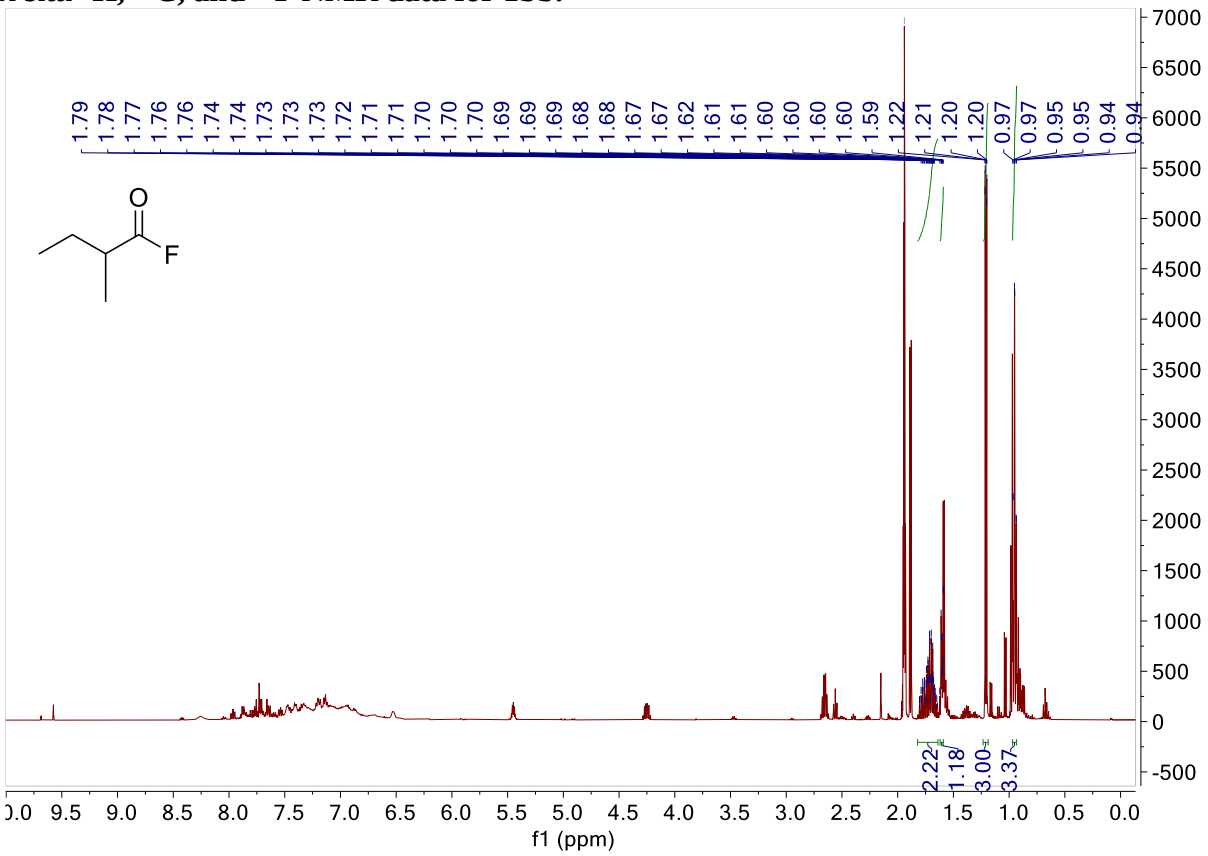

52.54
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
110
90
70
50
30
10
-10
-30
-50
-70
-90
-110
f1 (ppm)

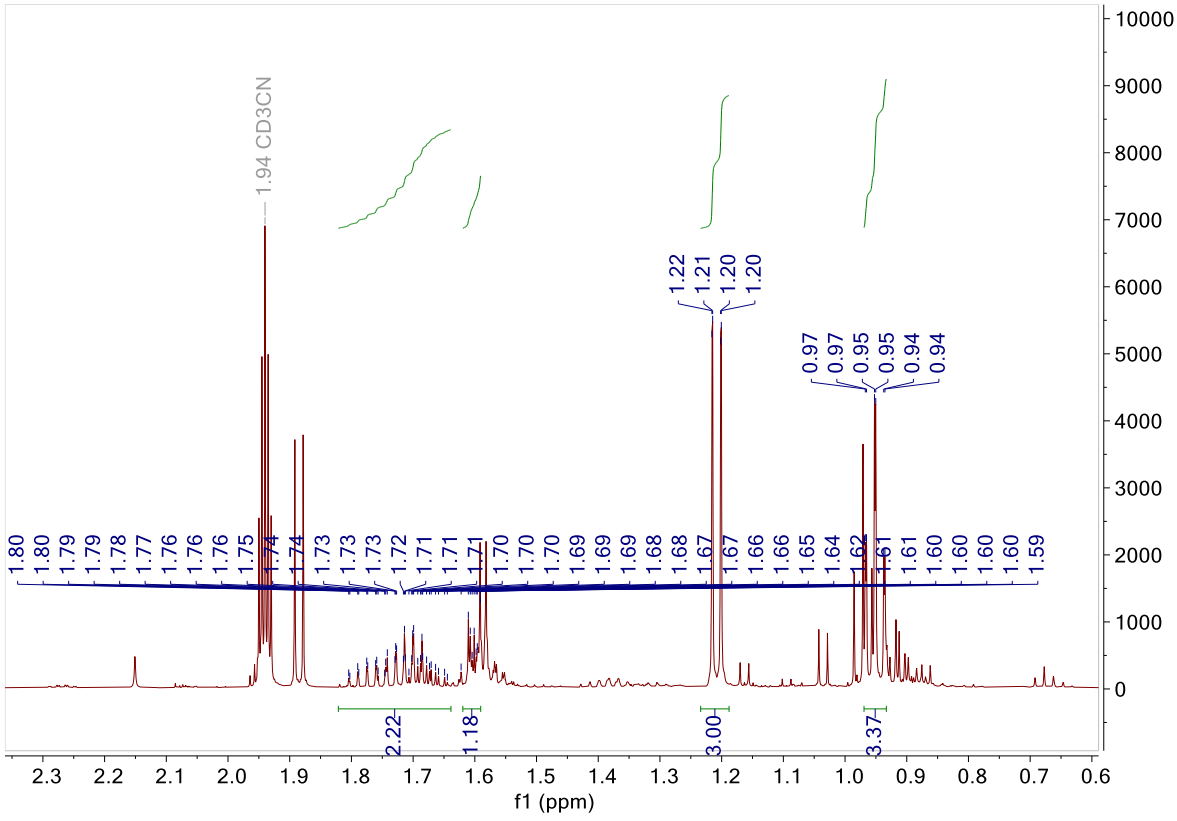
^{1}H and ^{13}C NMR data for 5aa.

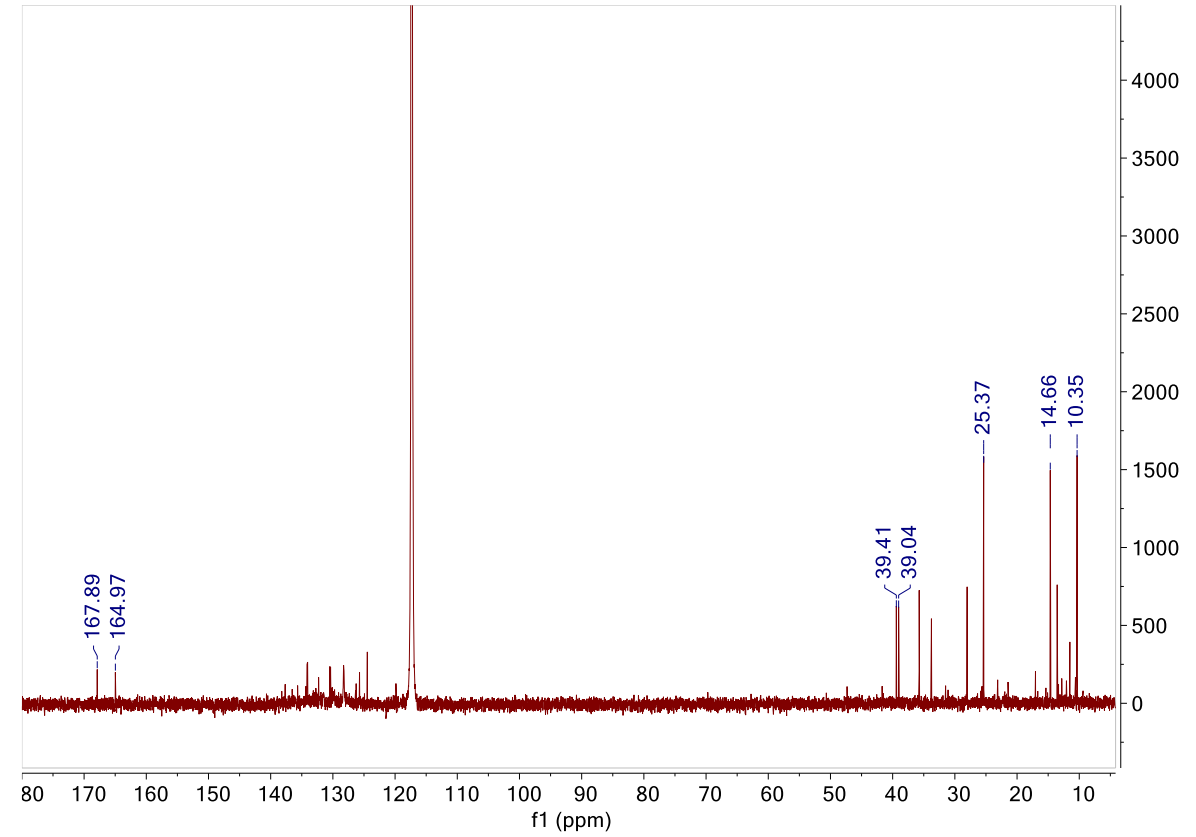


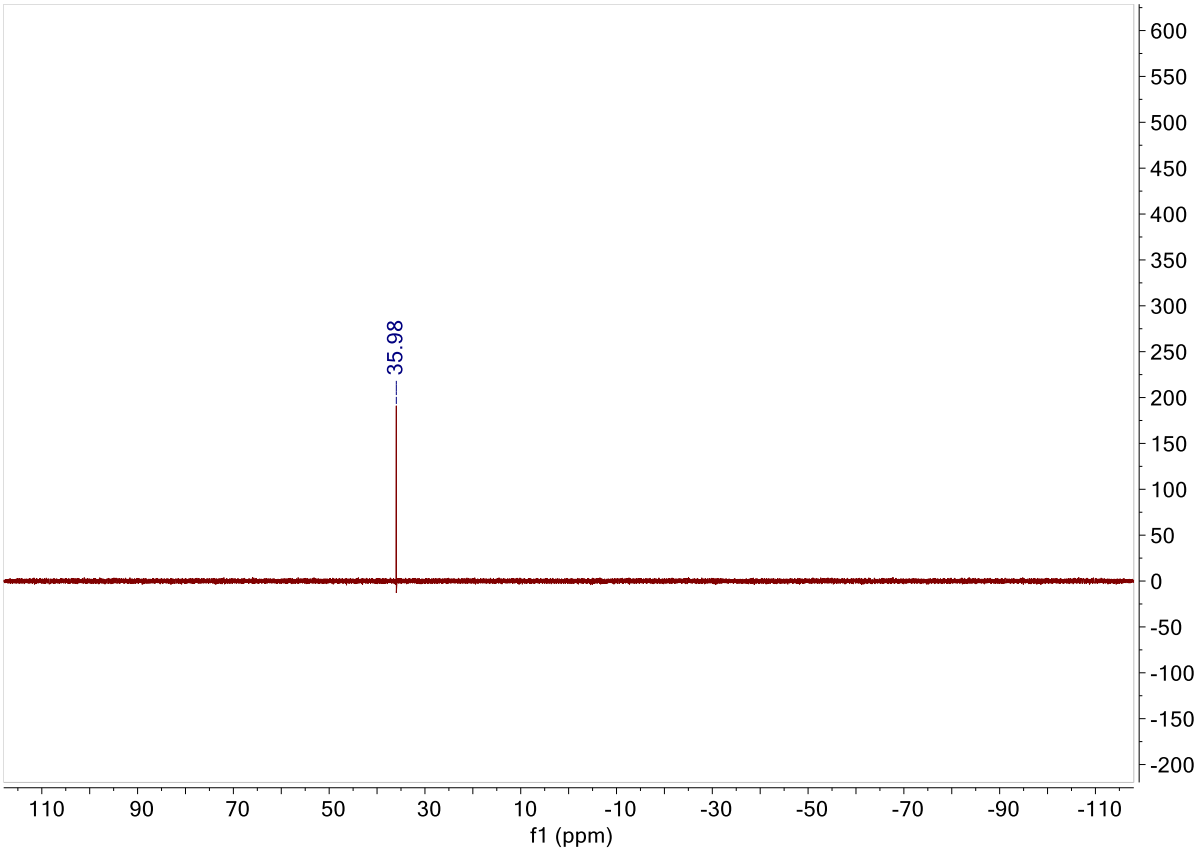


***In situ* ^{1}H, ^{13}C, and ^{19}F NMR data for 1bb.**

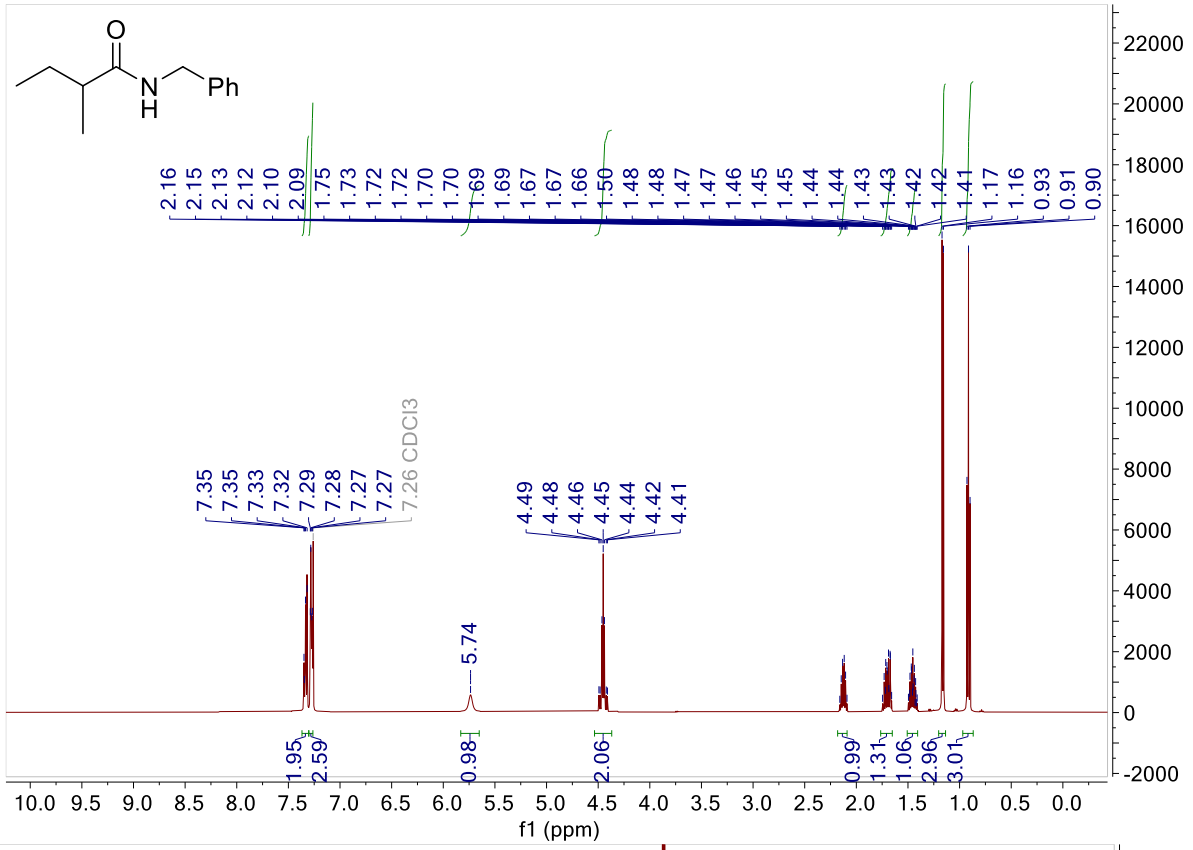


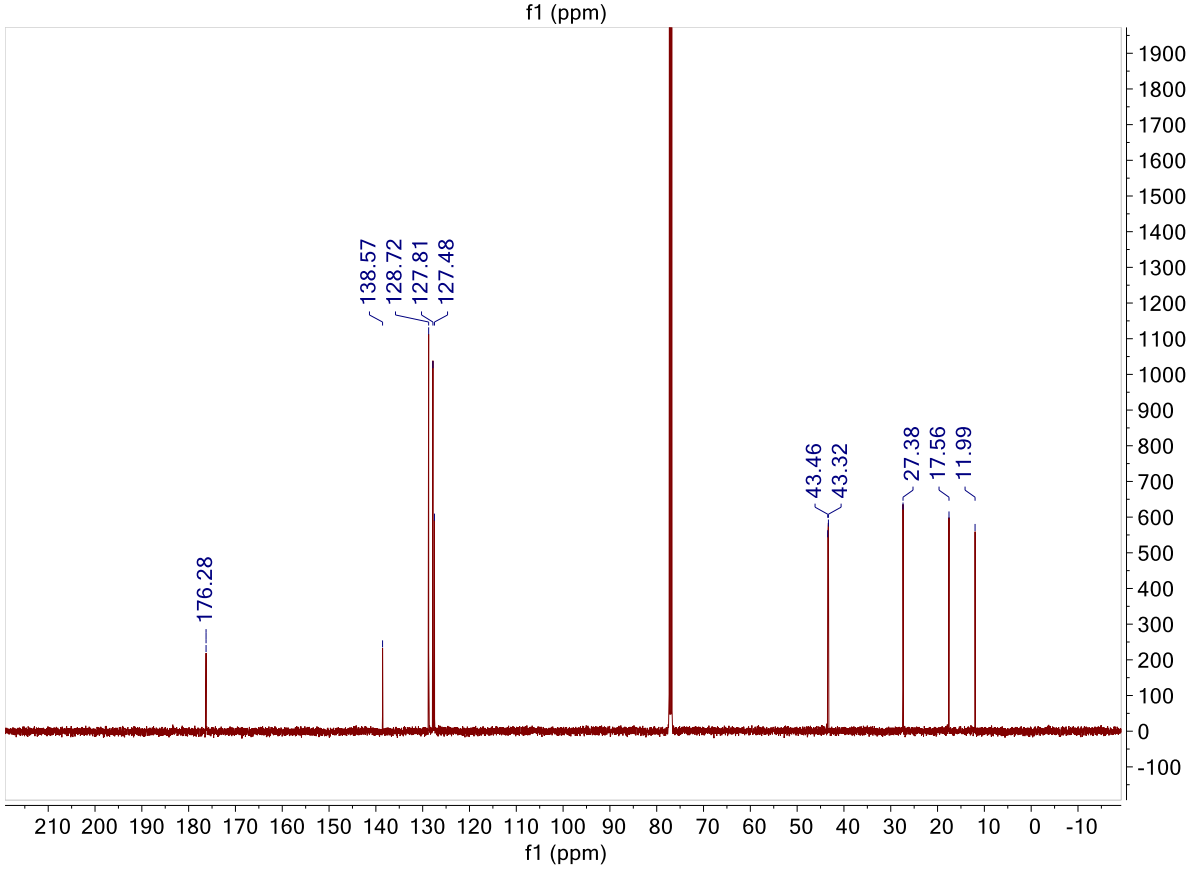



167.89
164.97
39.41
39.04
25.37
14.66
10.35
4000
3500
3000
2500
2000
1500
1000
500
0
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

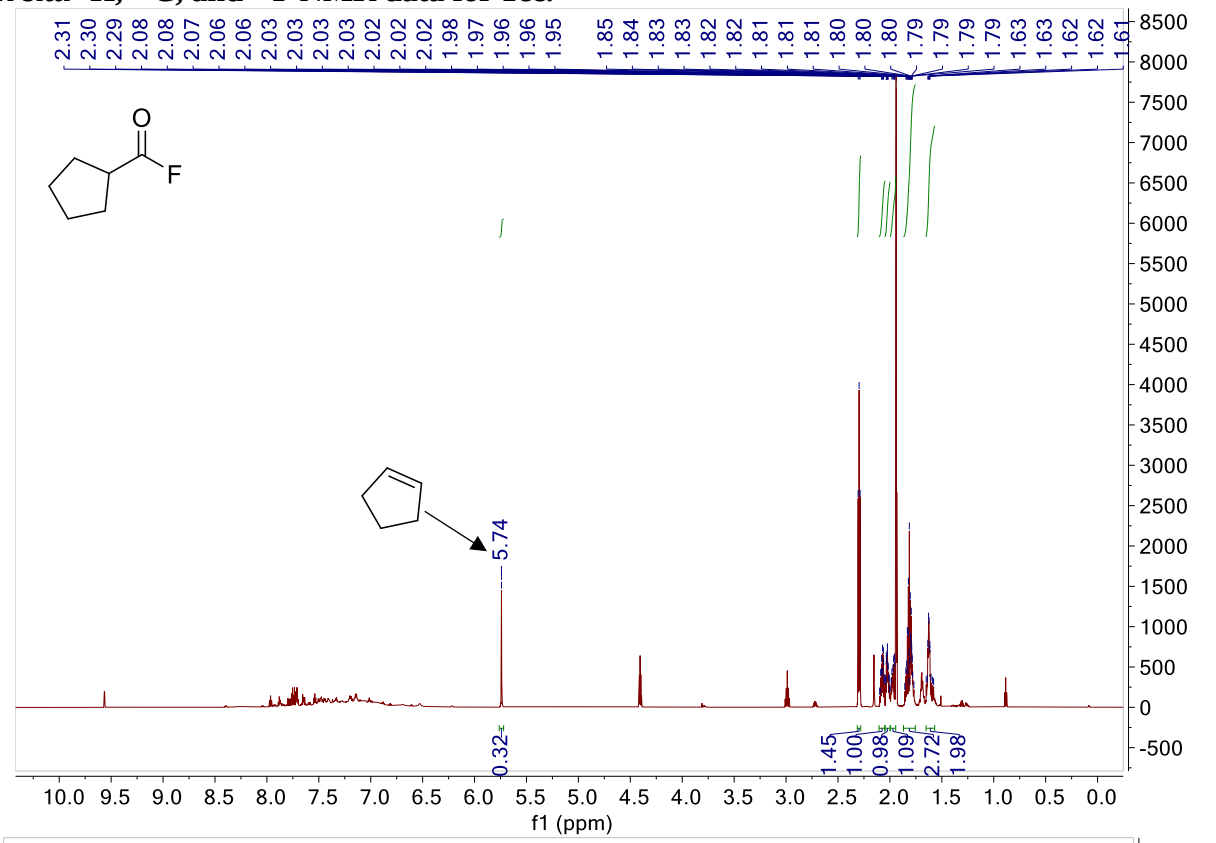

35.98
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
110 90 70 50 30 10 -10 -30 -50 -70 -90 -110
f1 (ppm)

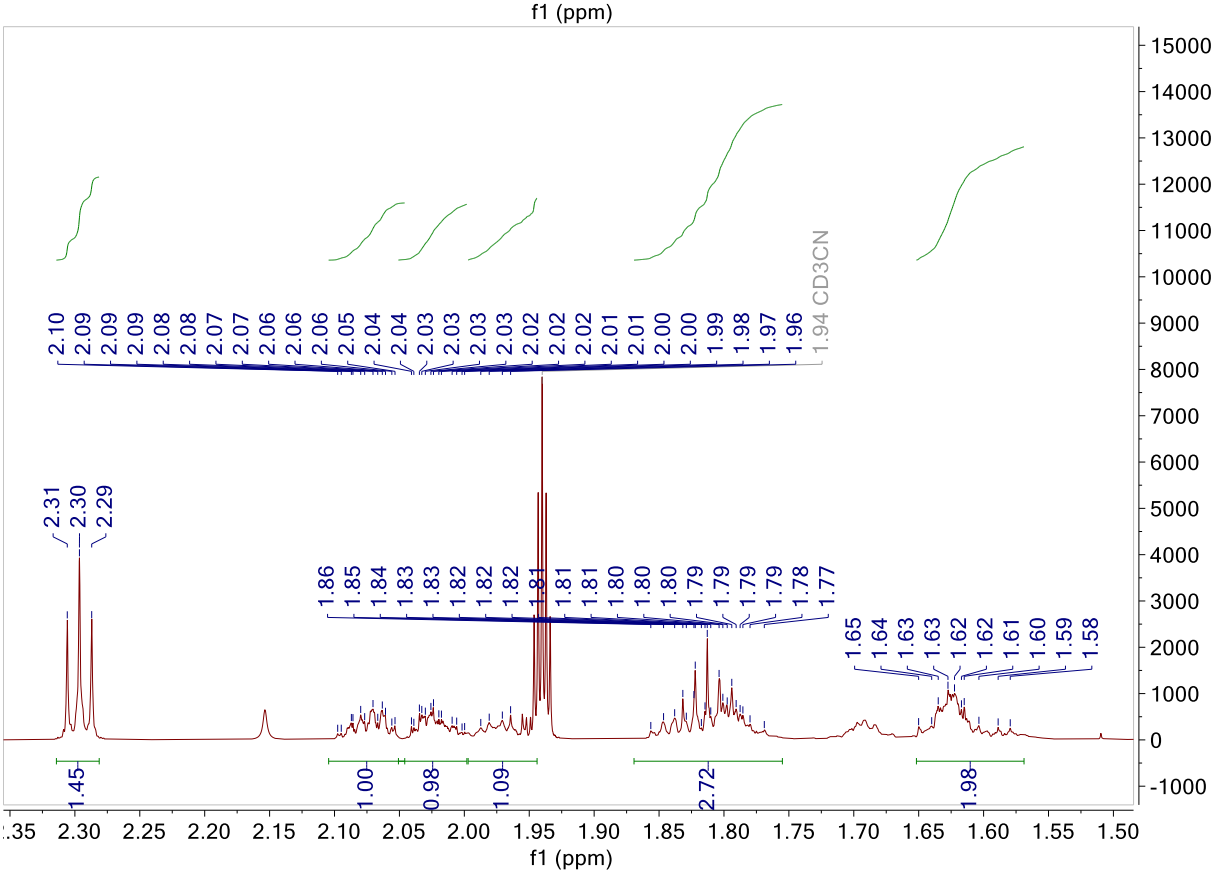
^{1}H and ^{13}C NMR data for 5bb.

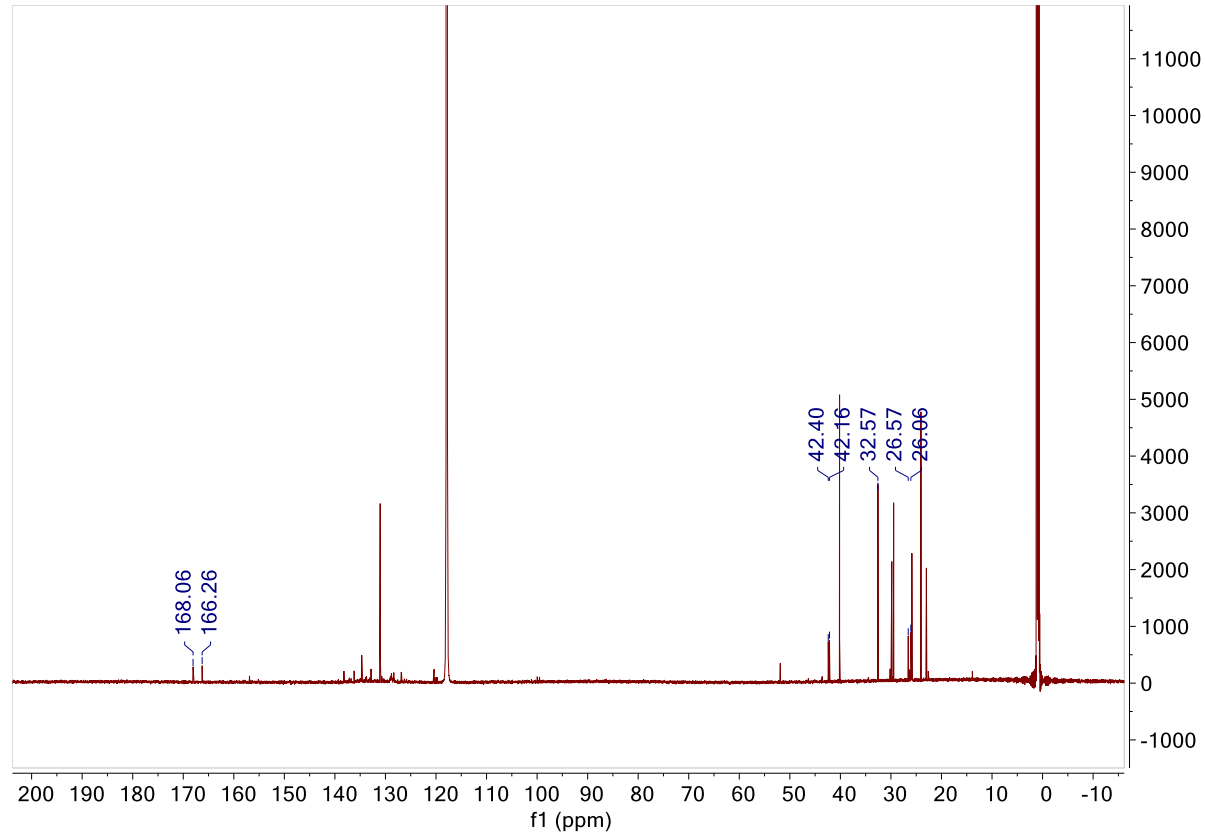


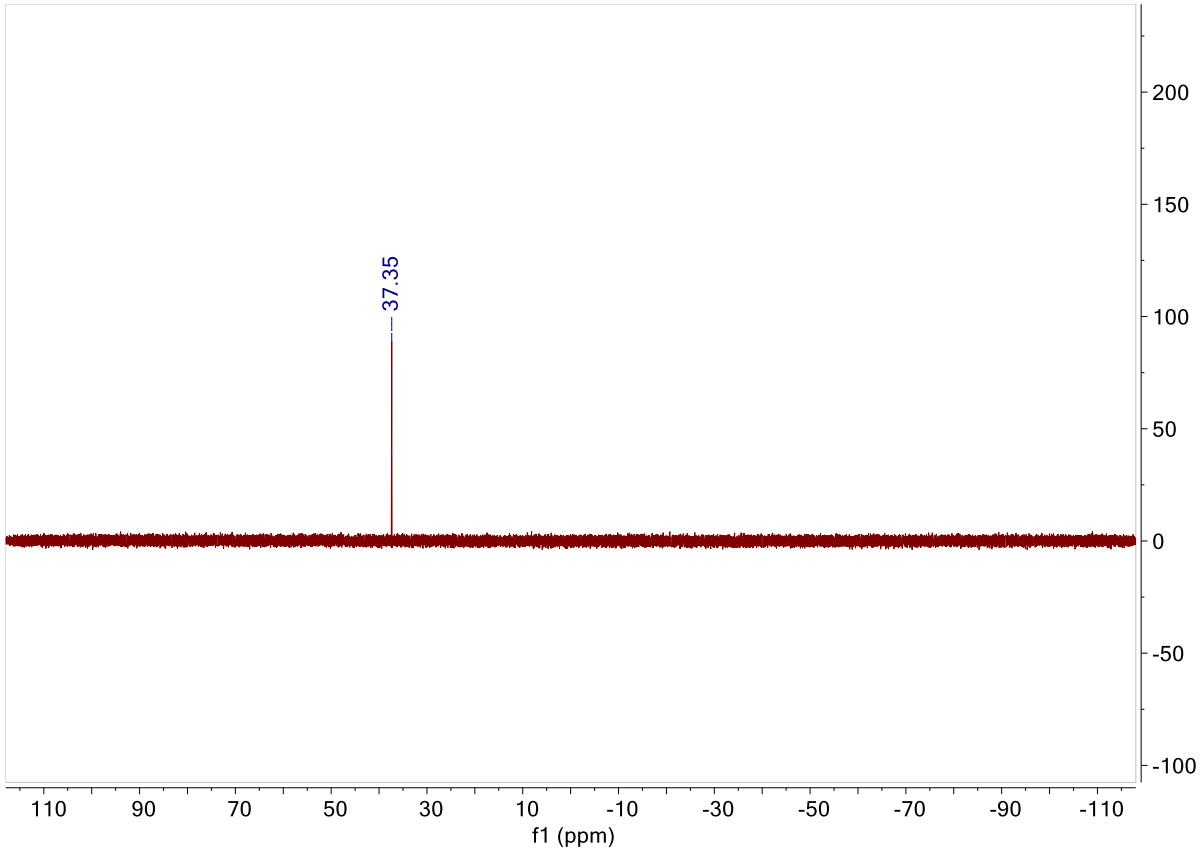


***In situ* ^{1}H, ^{13}C, and ^{19}F NMR data for 1cc.**

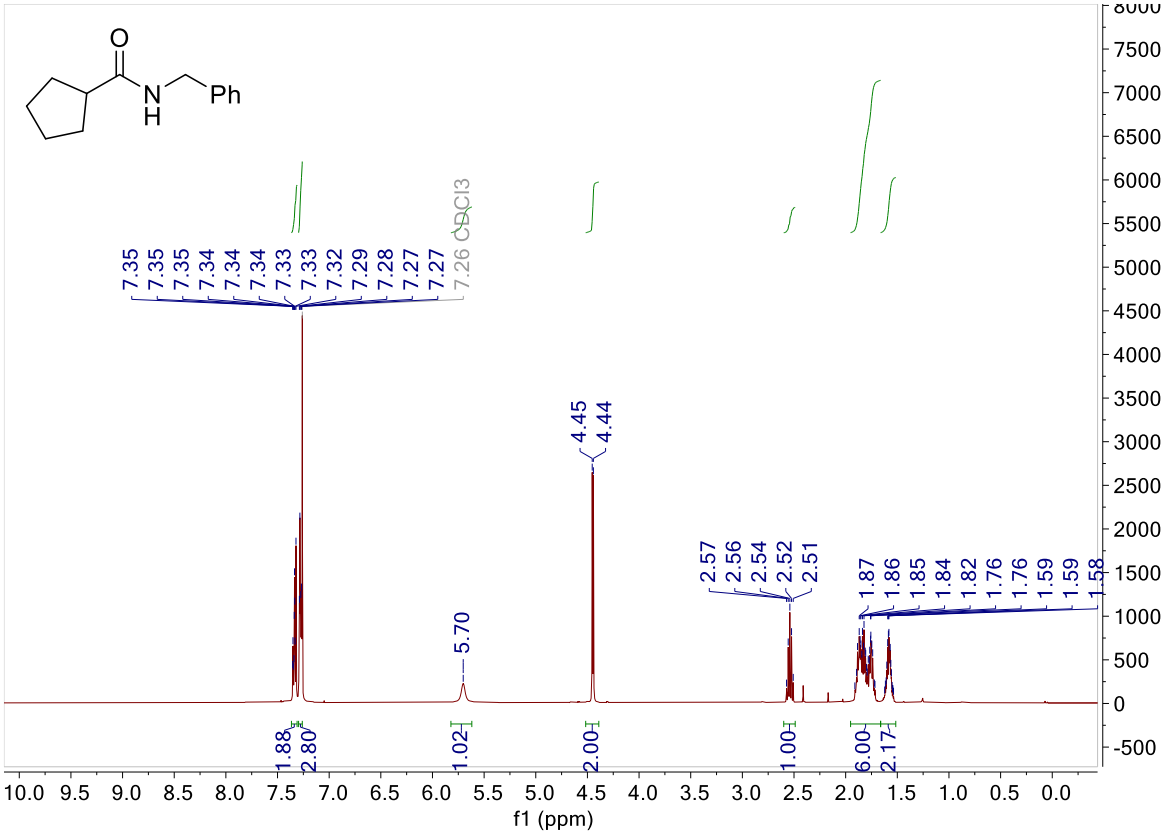


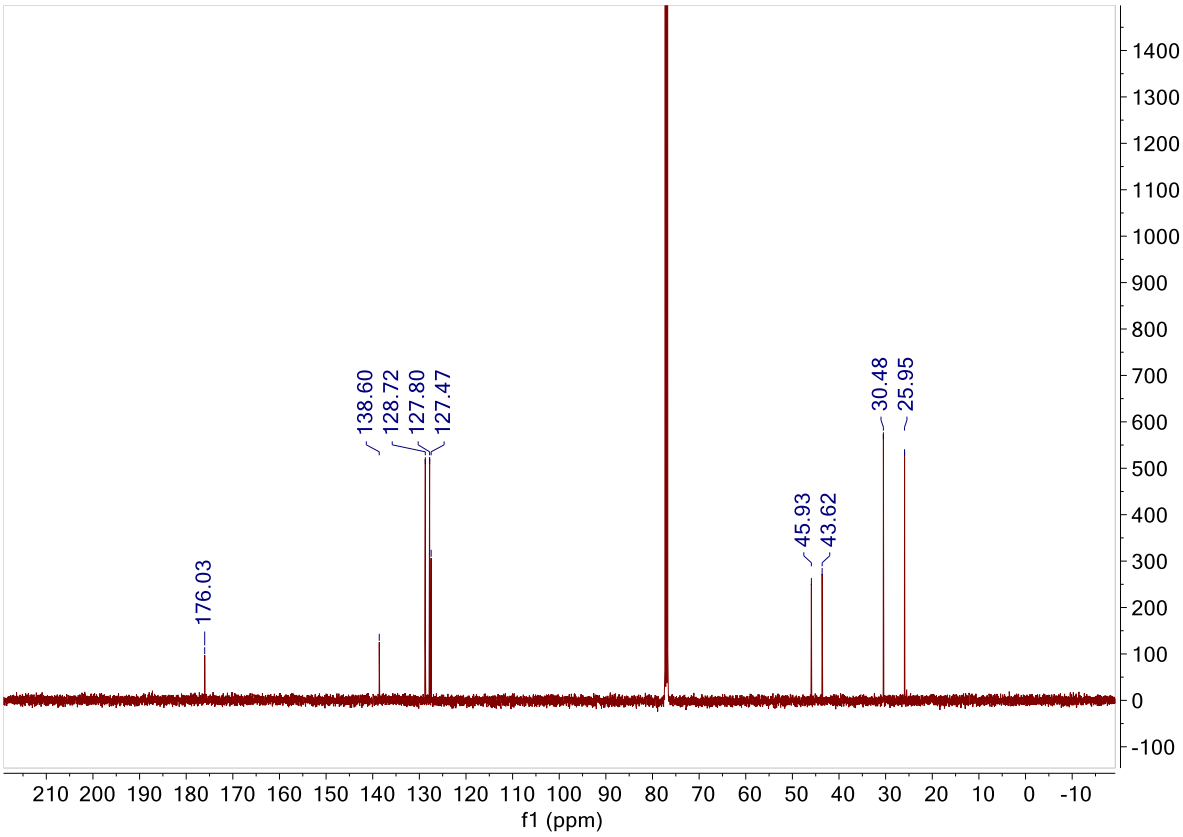



168.06
166.26
42.40
42.16
32.57
26.57
26.06
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

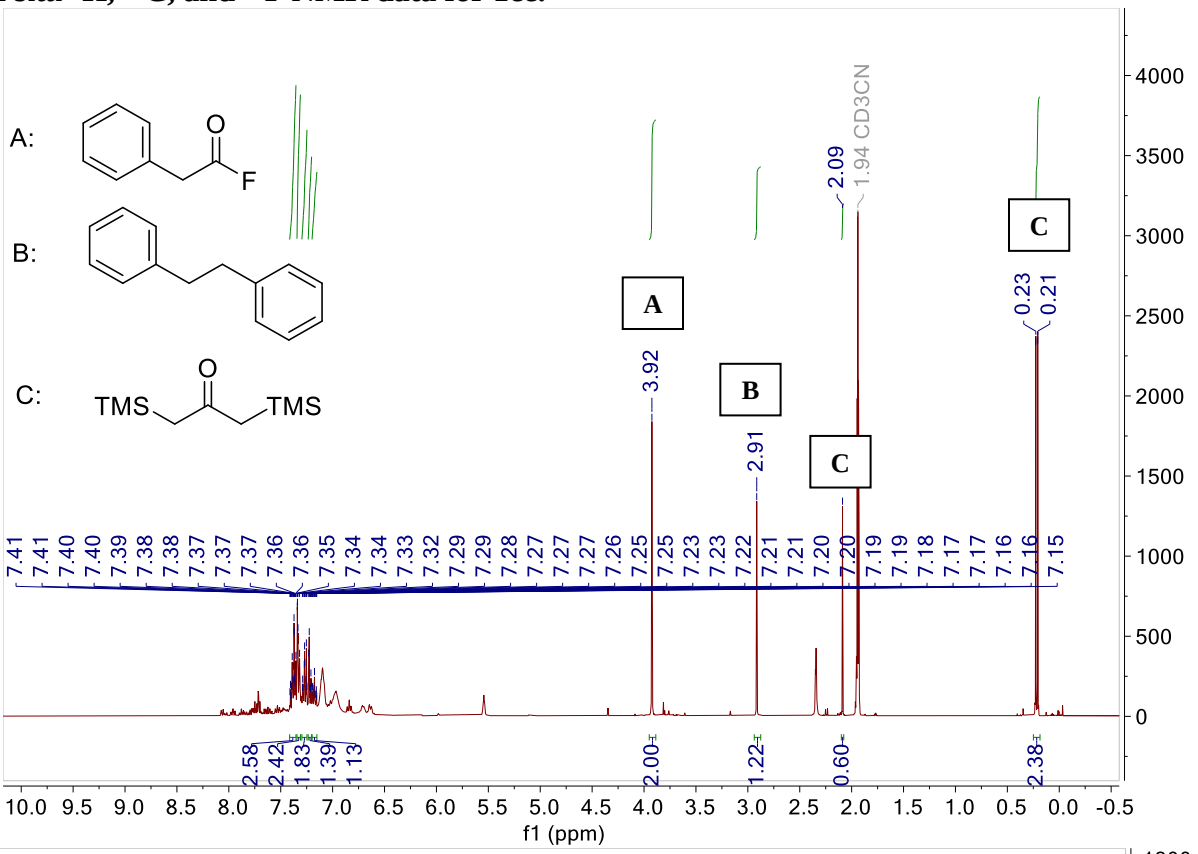

37.35
200
150
100
50
0
-50
-100
110 90 70 50 30 10 -10 -30 -50 -70 -90 -110
f1 (ppm)

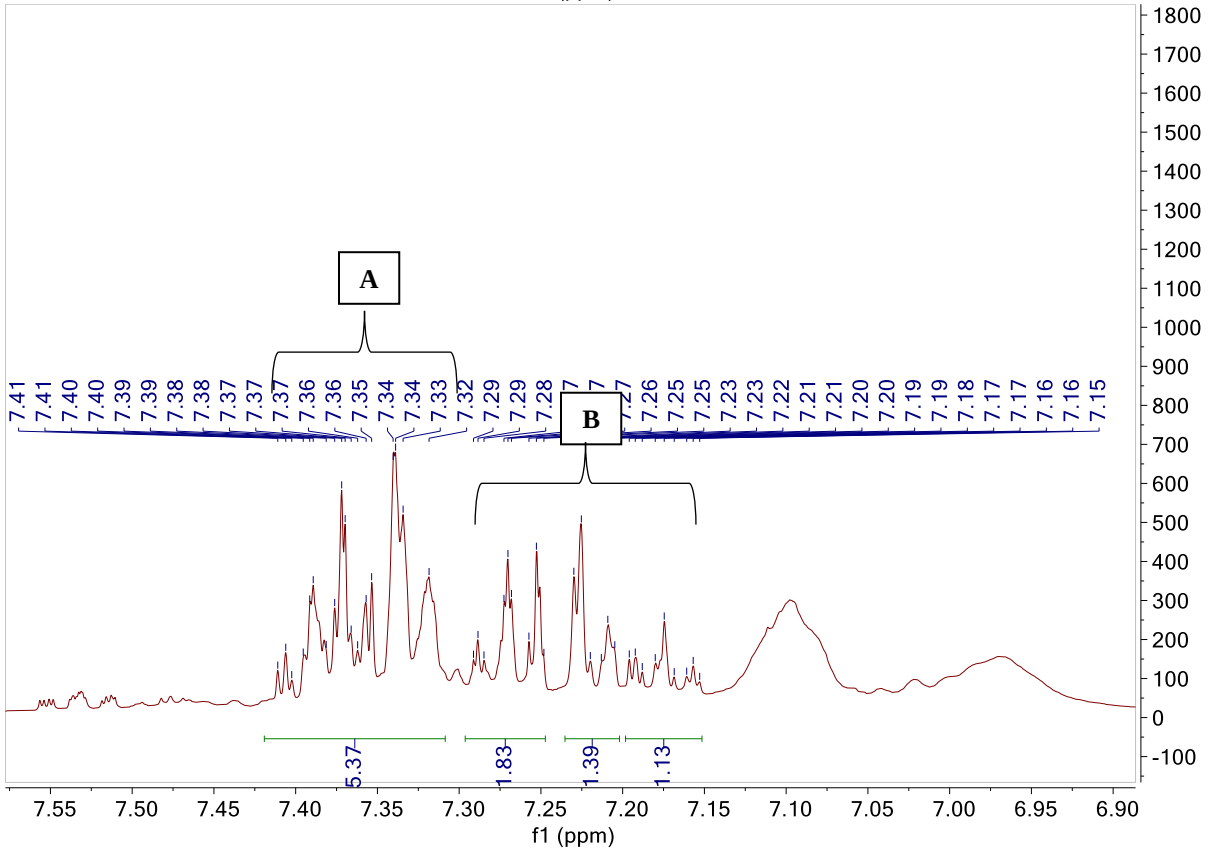
^{1}H and ^{13}C NMR data for 5cc.

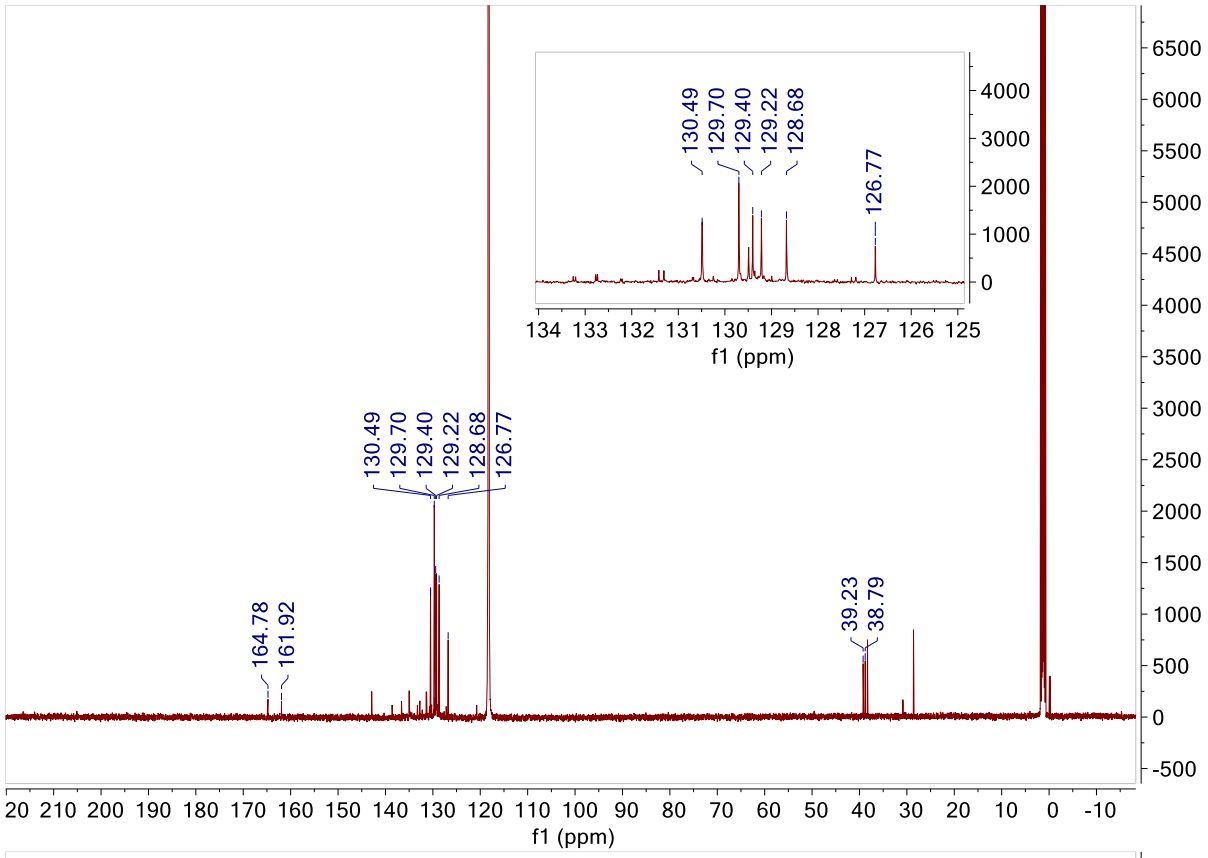


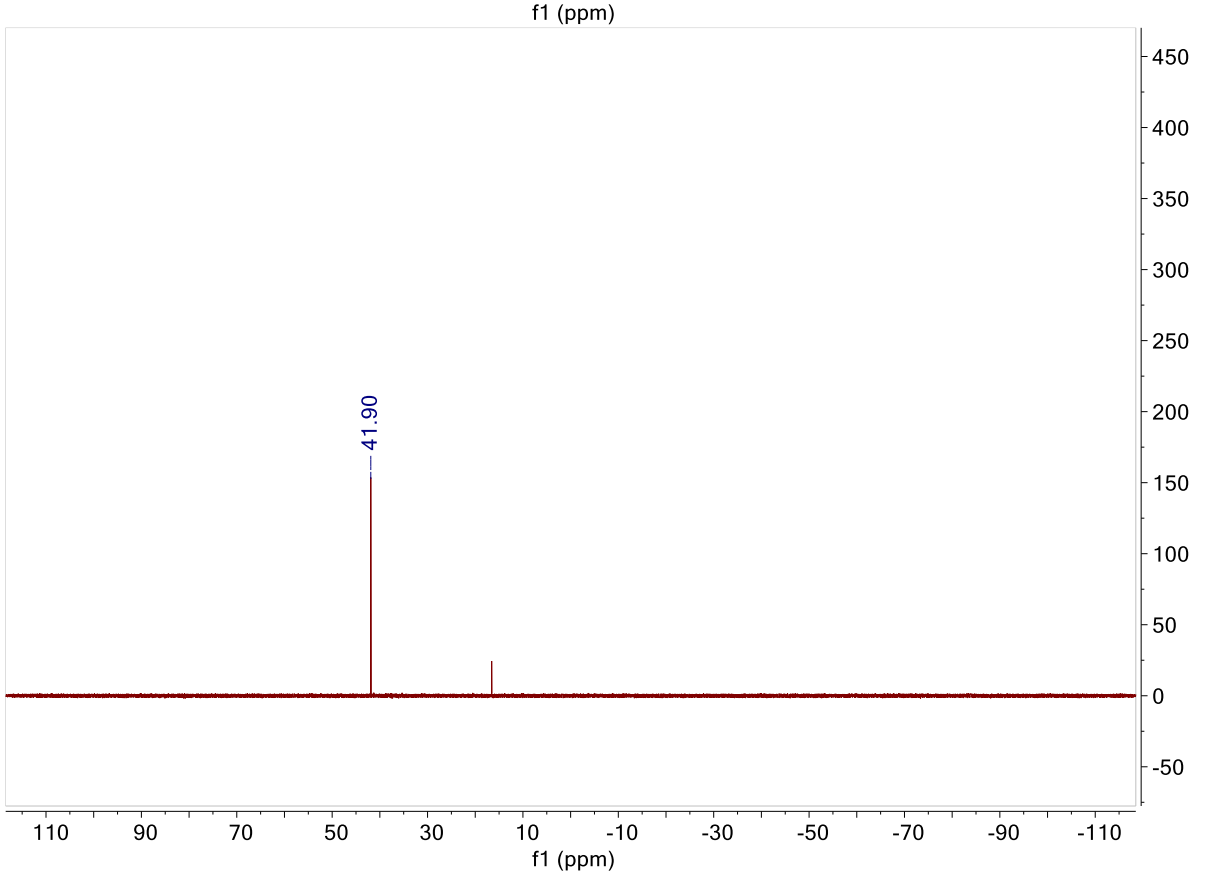


***In situ* ^{1}H, ^{13}C, and ^{19}F NMR data for 1ee.**

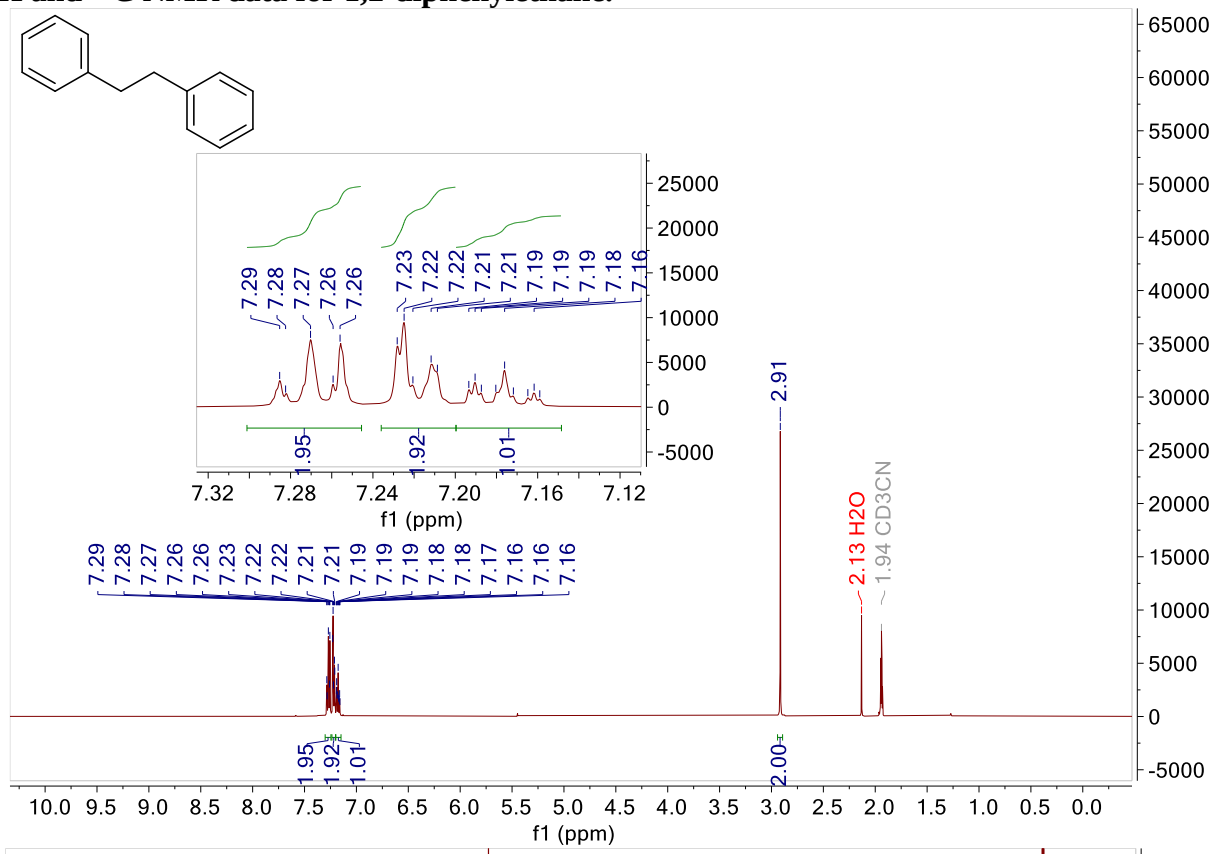


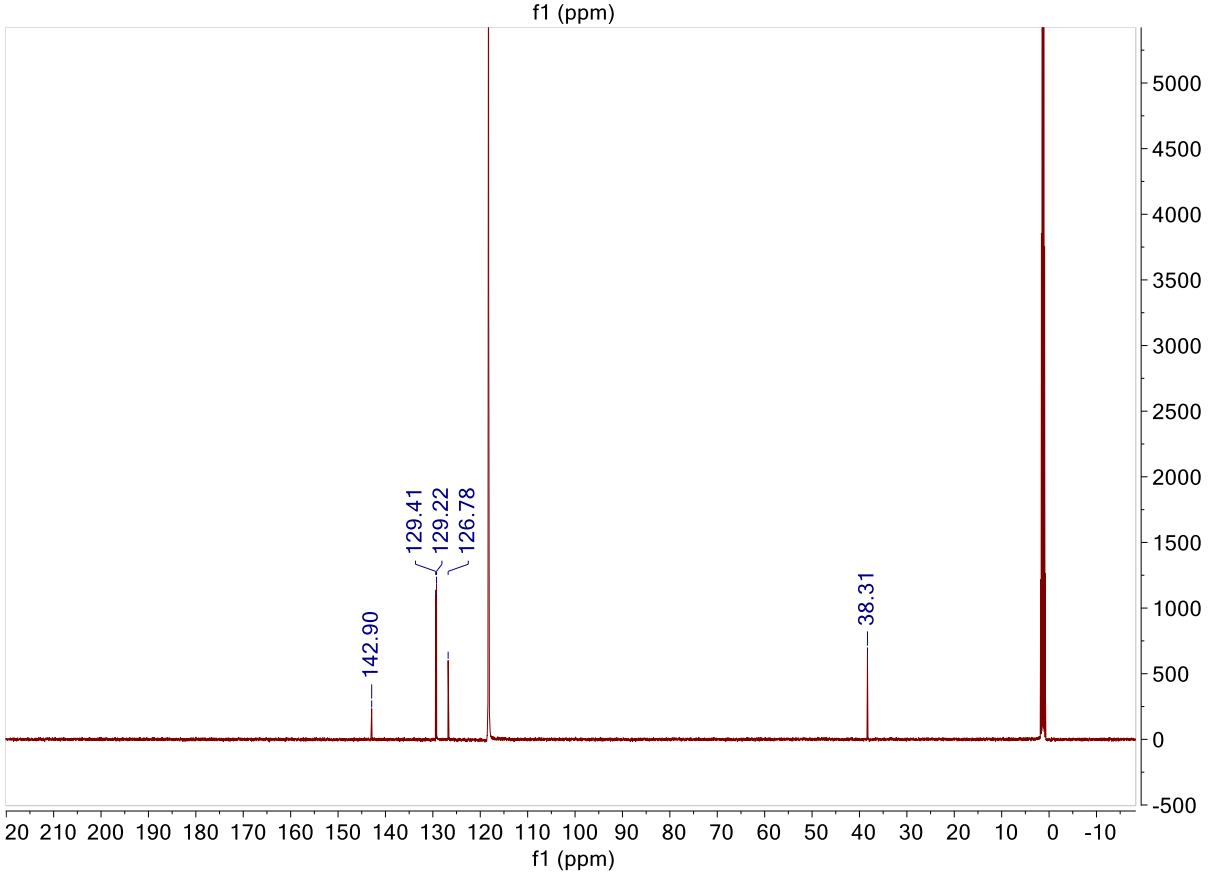



130.49
129.70
129.40
129.22
128.68
126.77
f1 (ppm)
164.78
161.92
39.23
38.79
f1 (ppm)

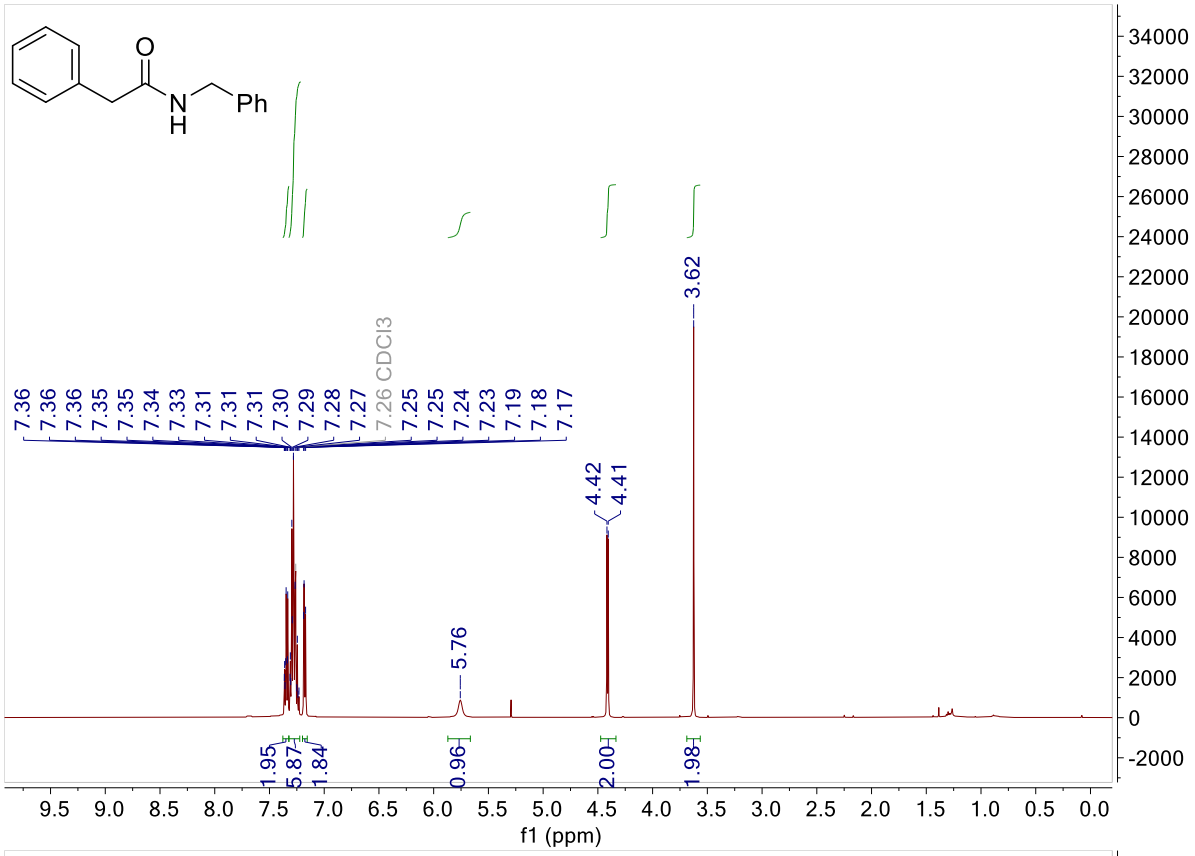

41.90
f1 (ppm)

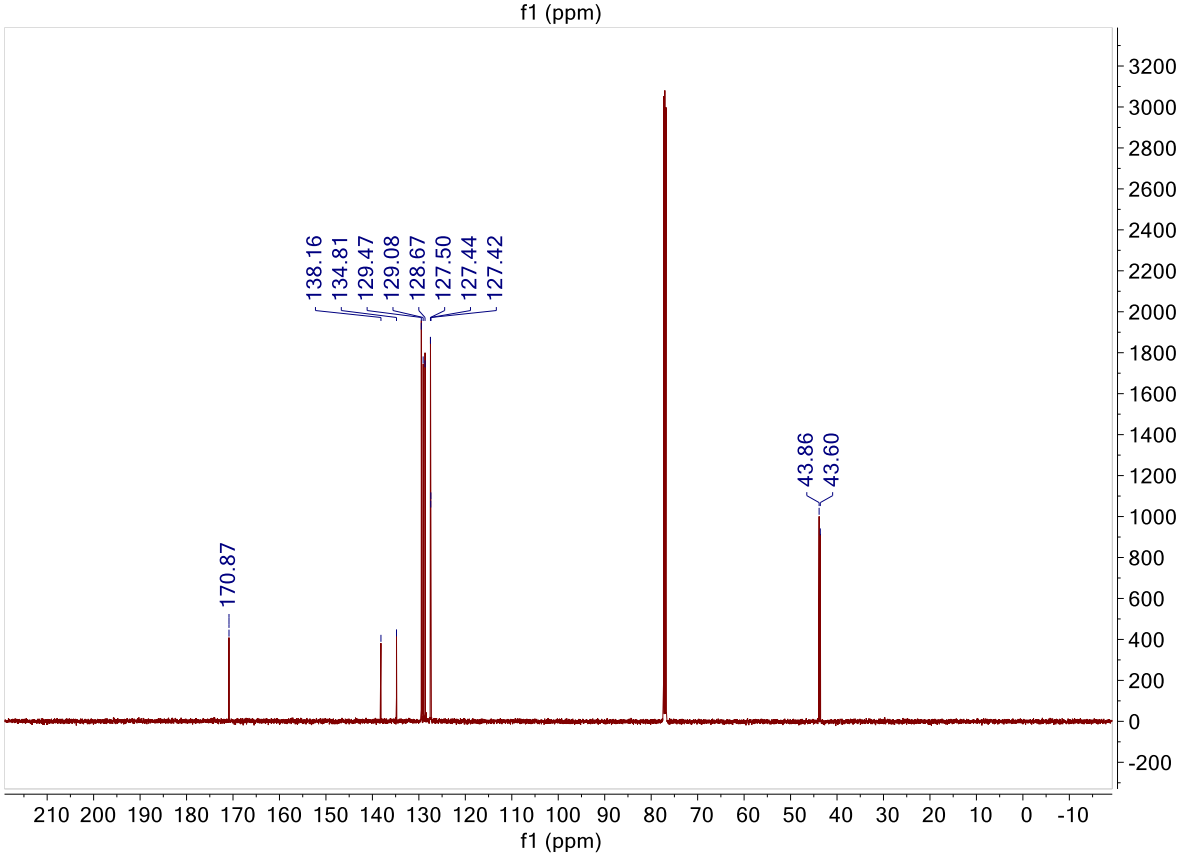
^{1}H and ^{13}C NMR data for 1,2-diphenylethane.



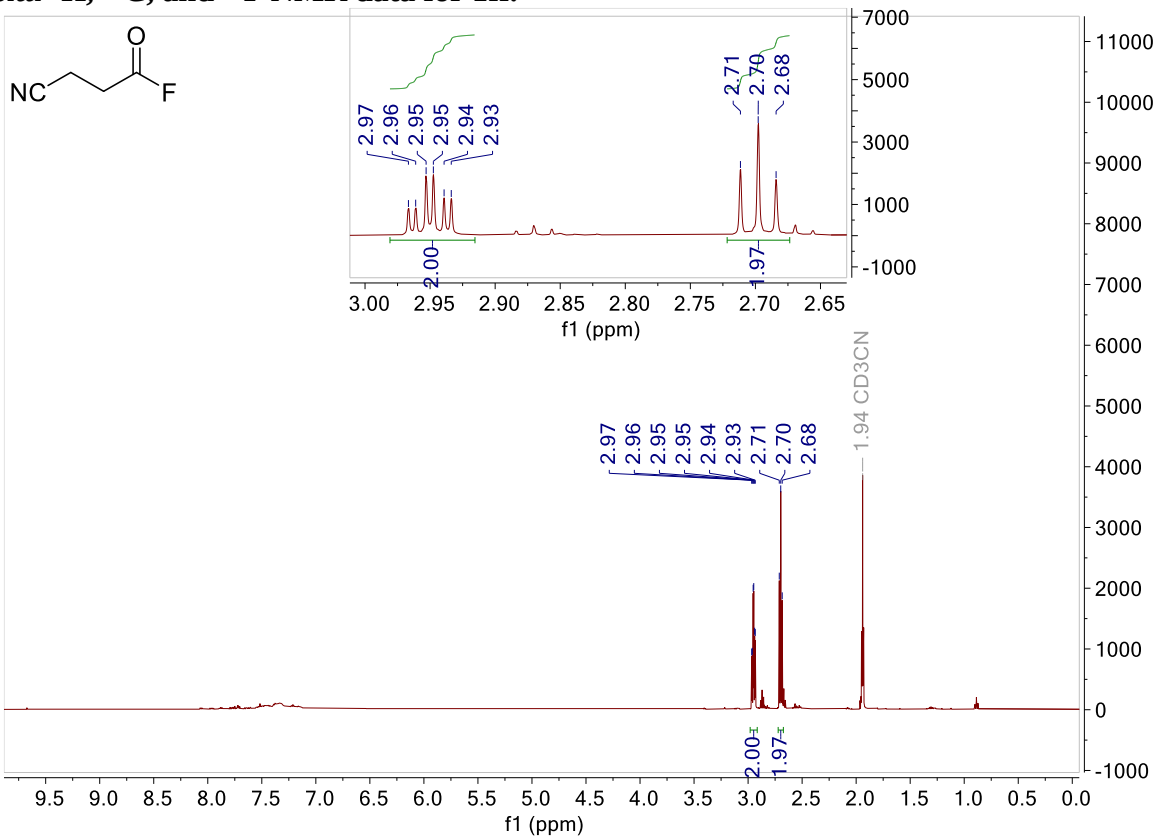


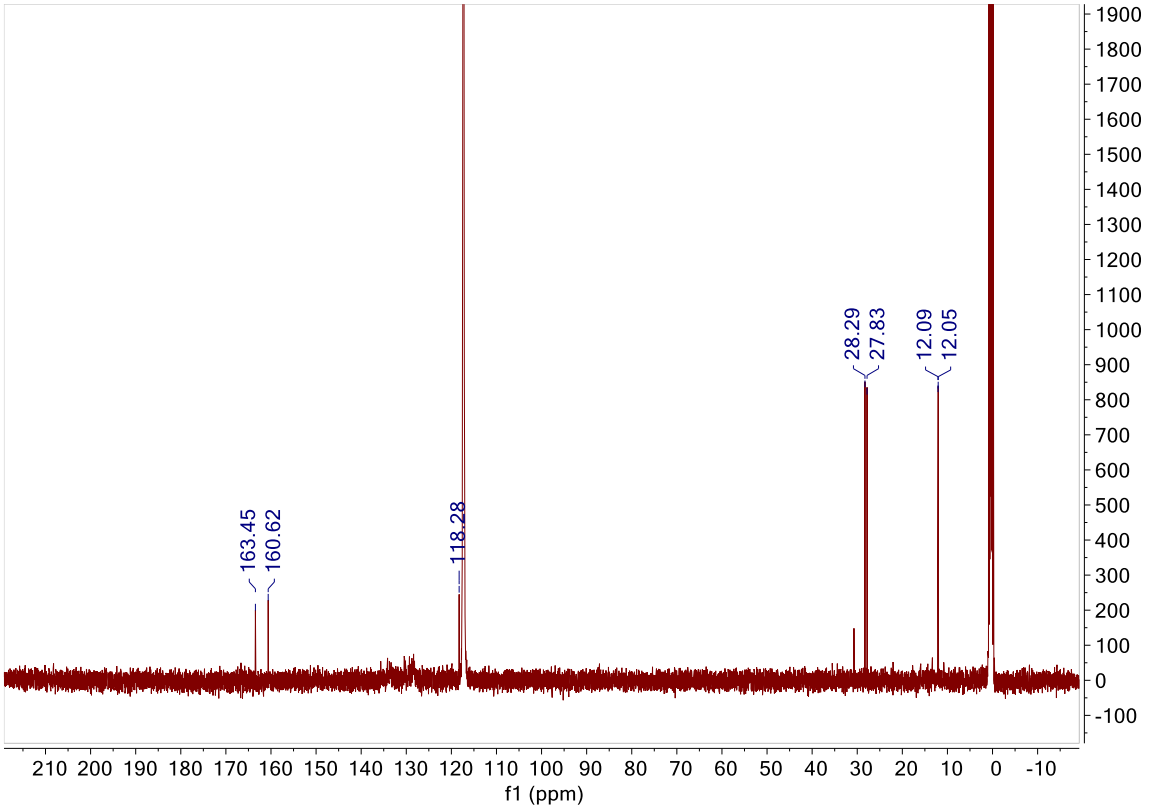
^{1}H and ^{13}C NMR data for 5ee.

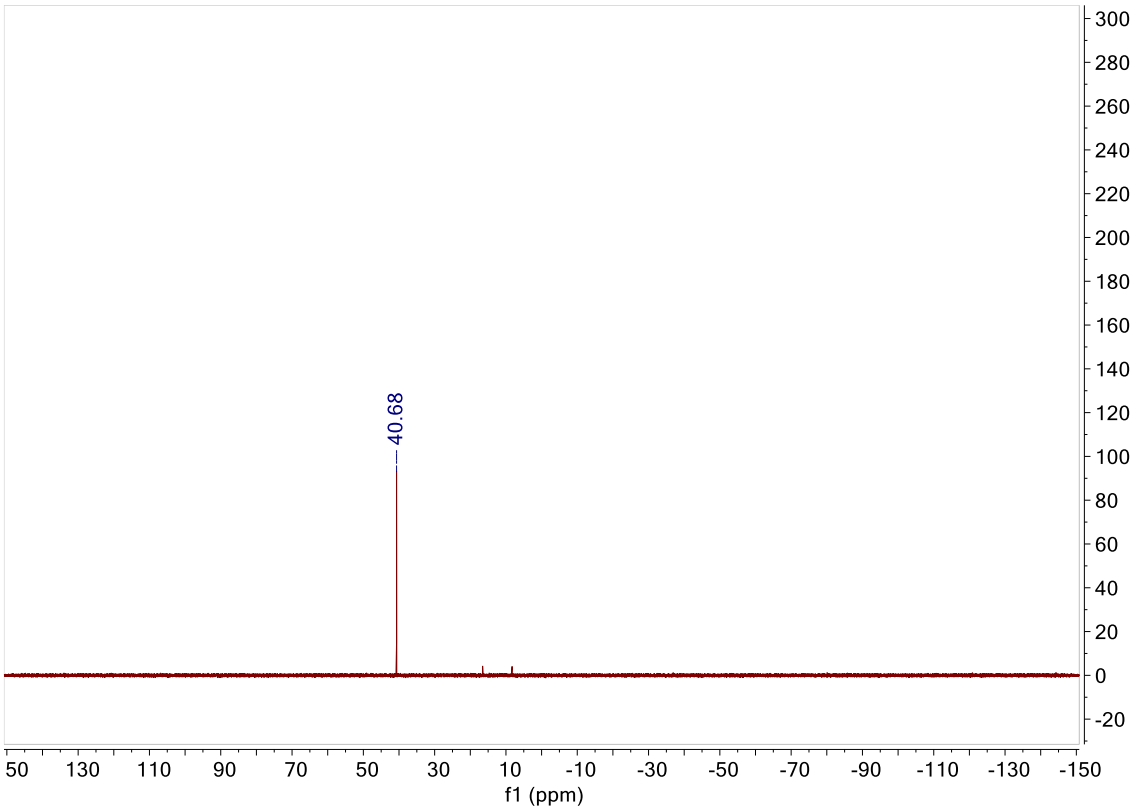




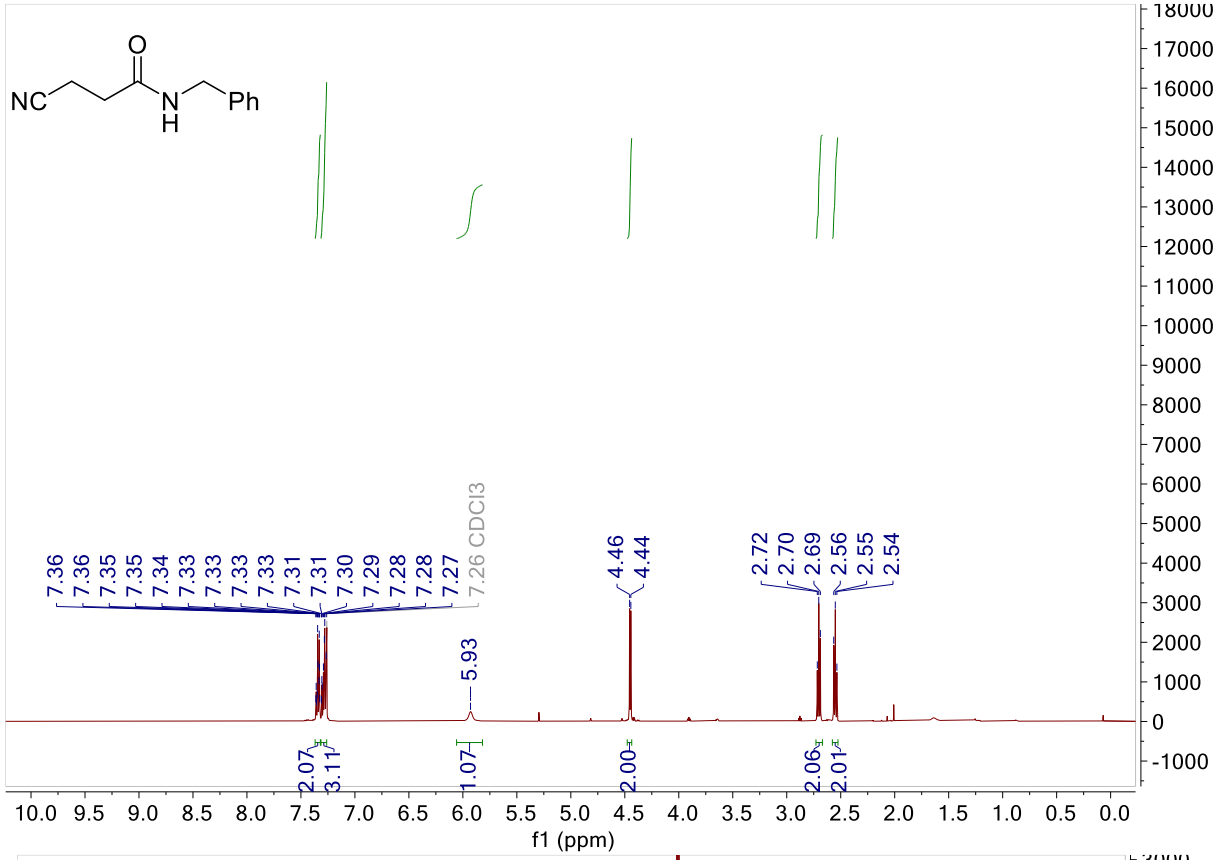
***In situ* ^{1}H, ^{13}C, and ^{19}F NMR data for 1ff.**

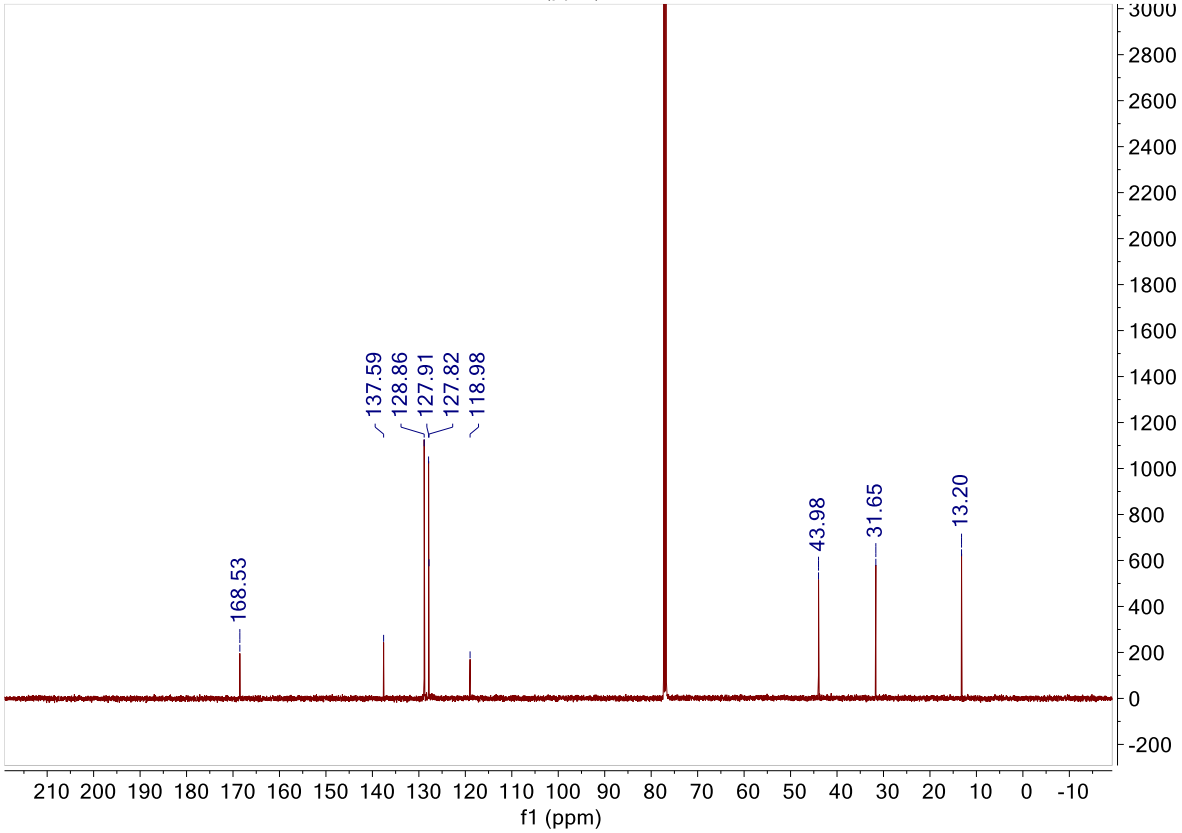




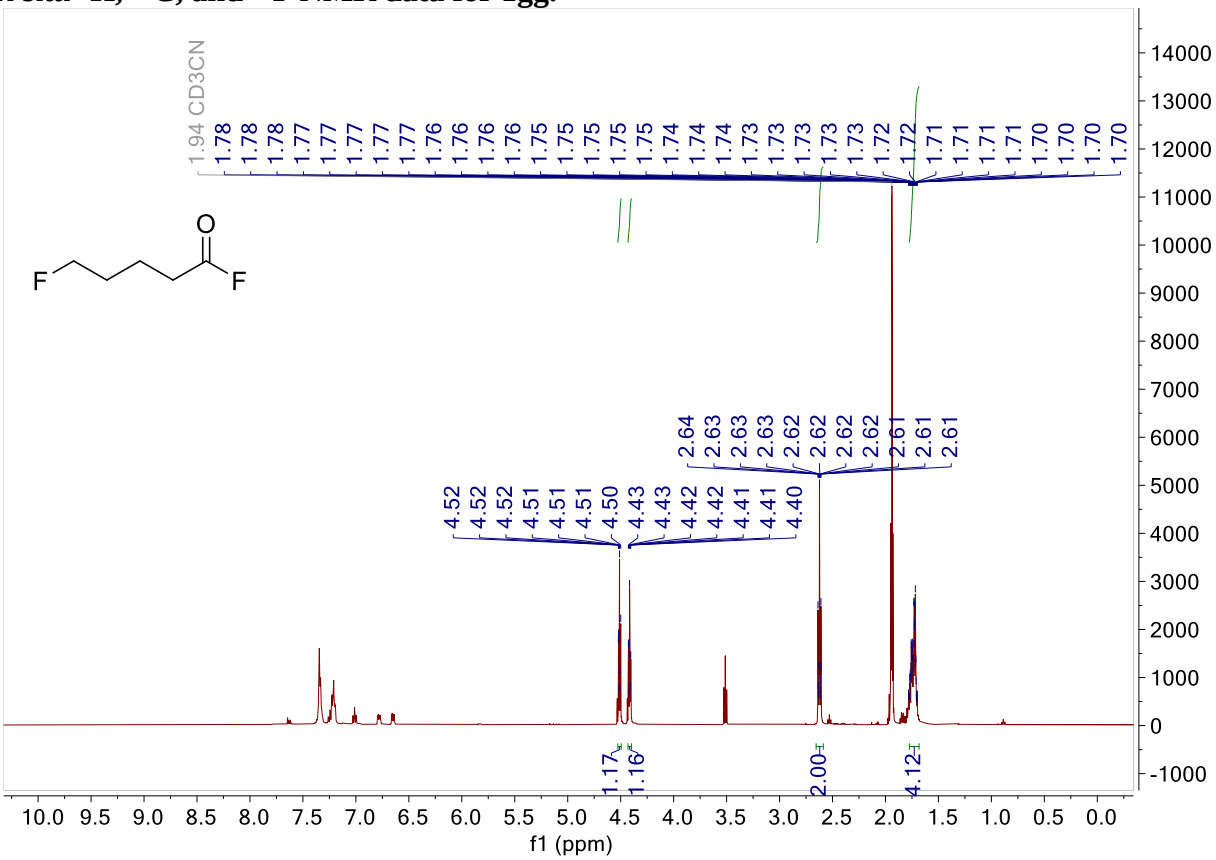

40.68
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
50
130
110
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
f1 (ppm)

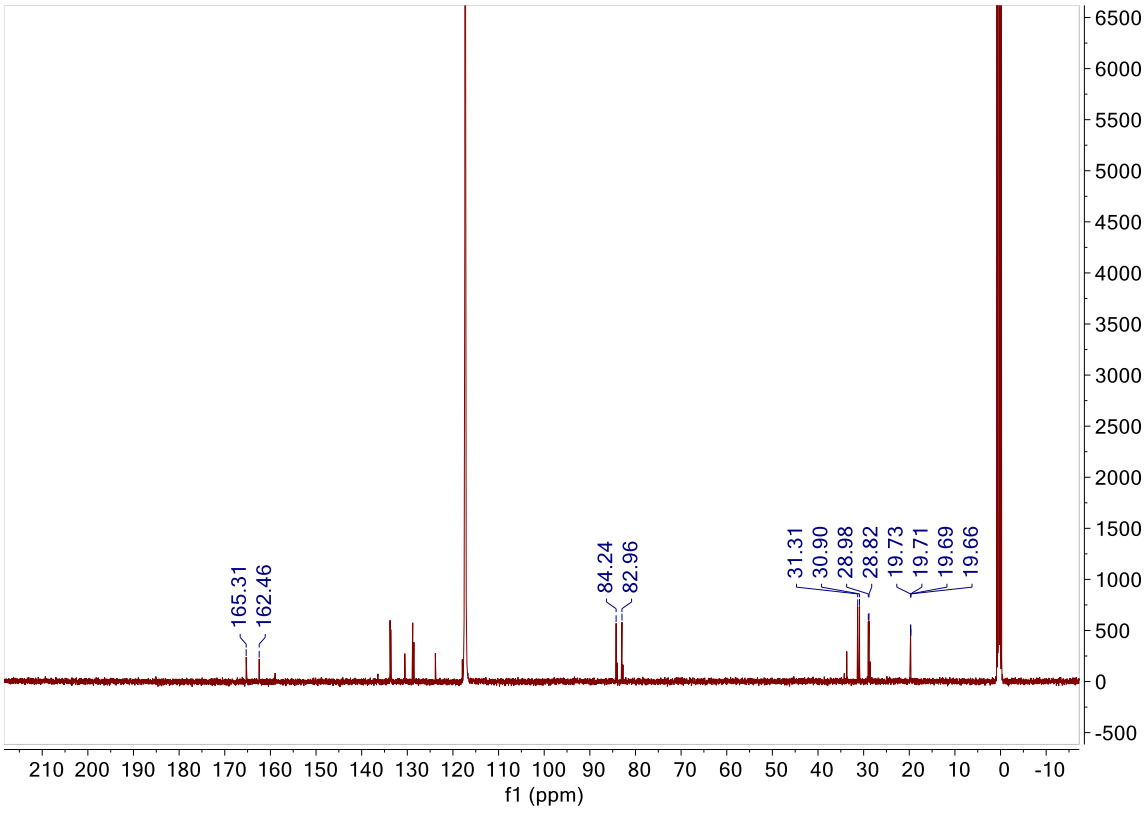
^{1}H and ^{13}C NMR data for 5ff.

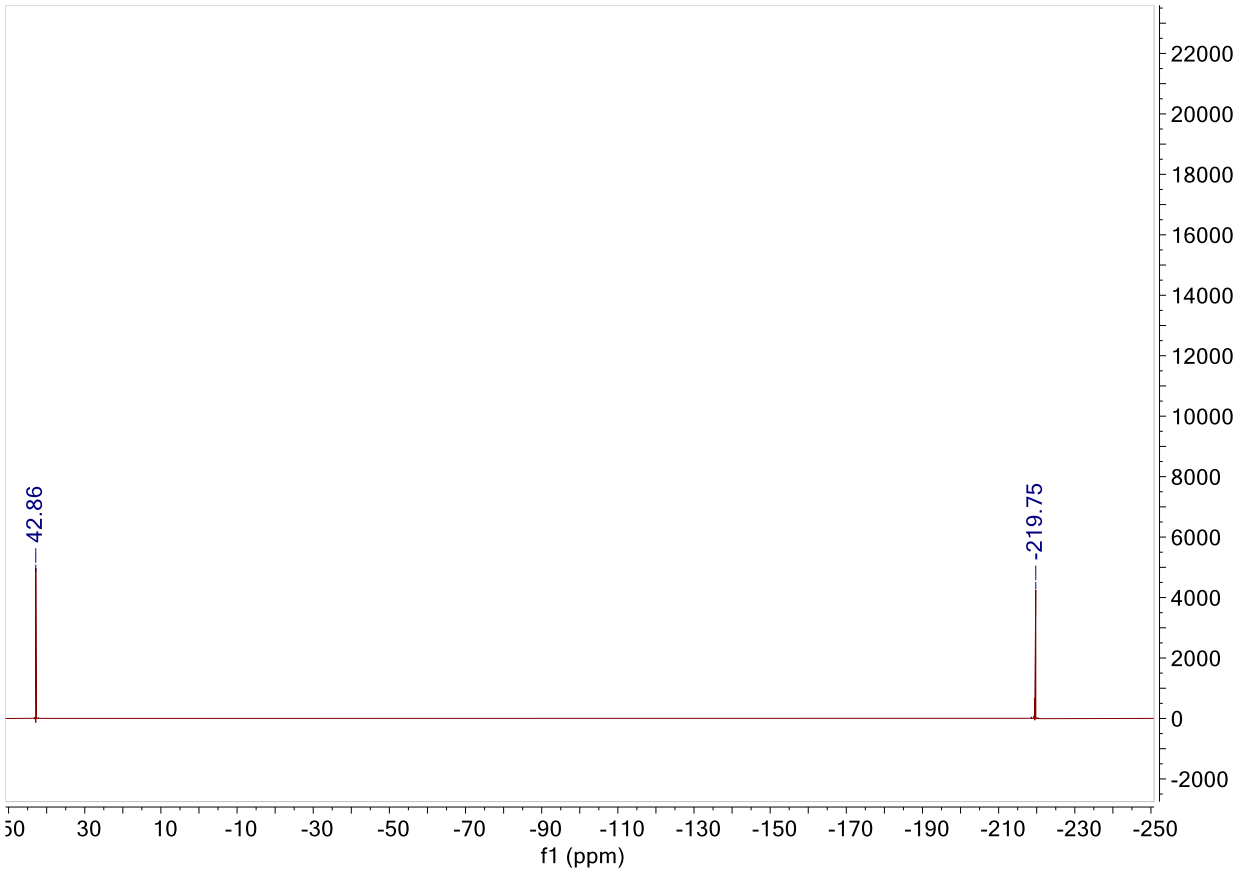




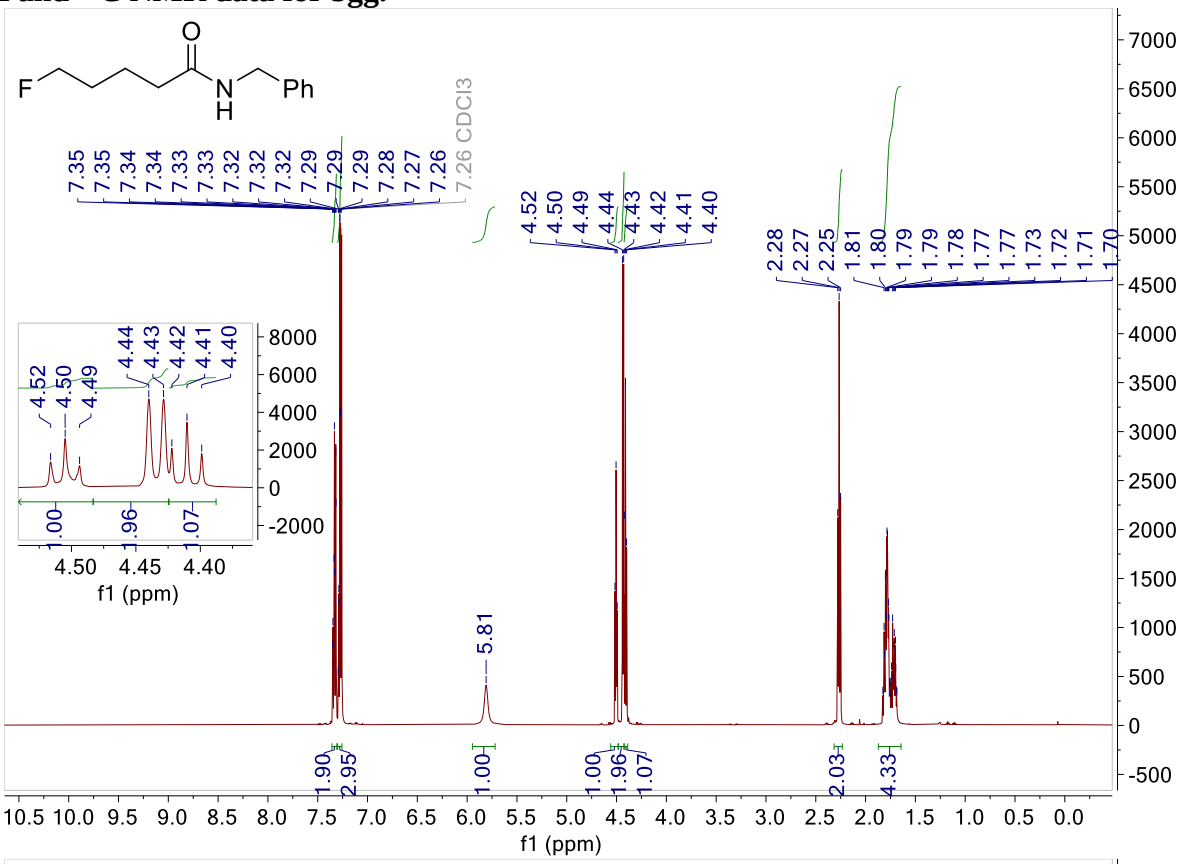
***In situ* ^{1}H, ^{13}C, and ^{19}F NMR data for 1gg.**

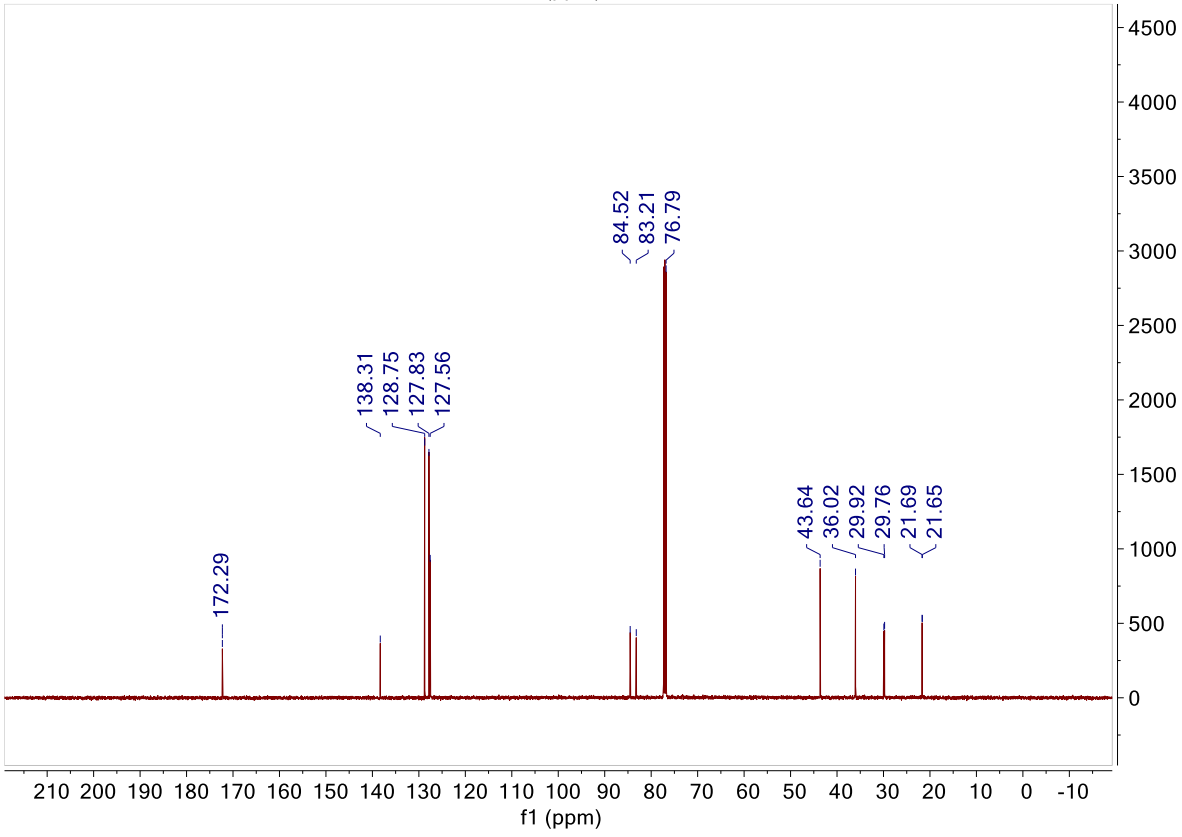




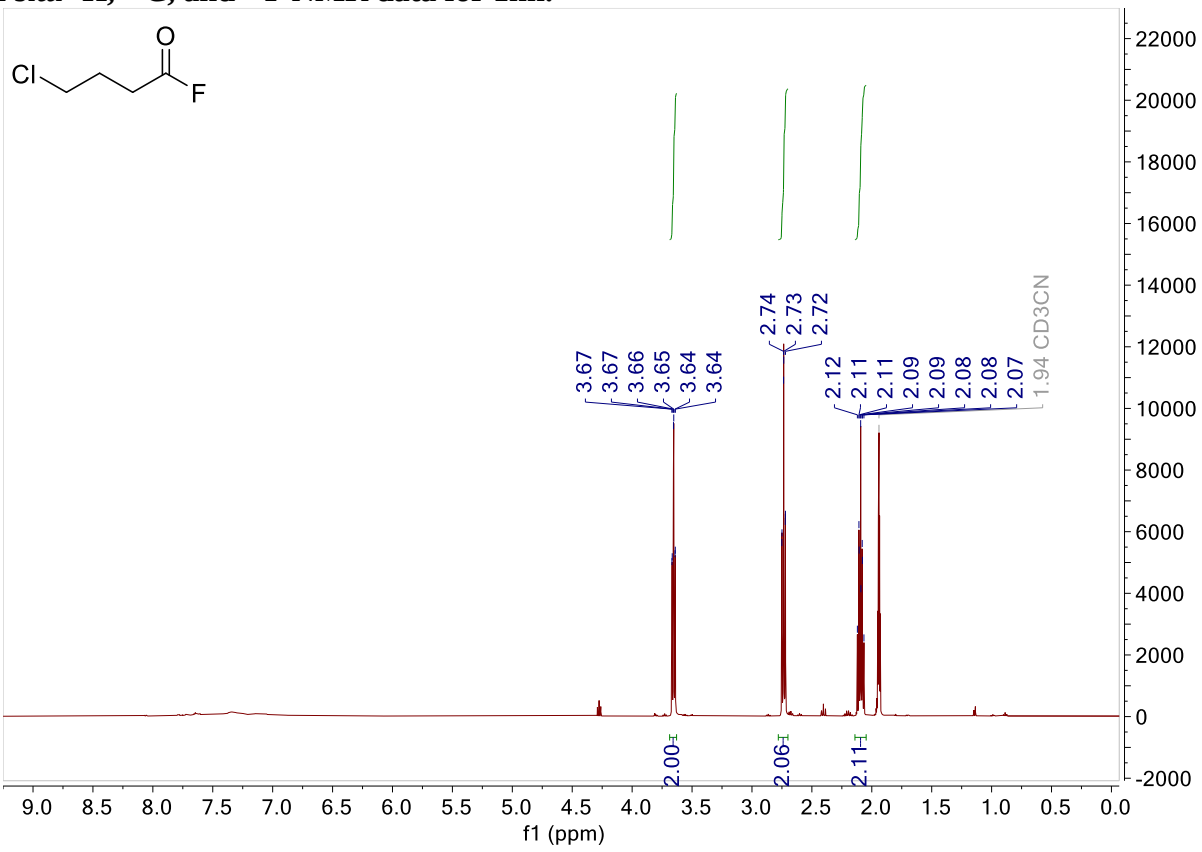

42.86
-219.75
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-250
f1 (ppm)

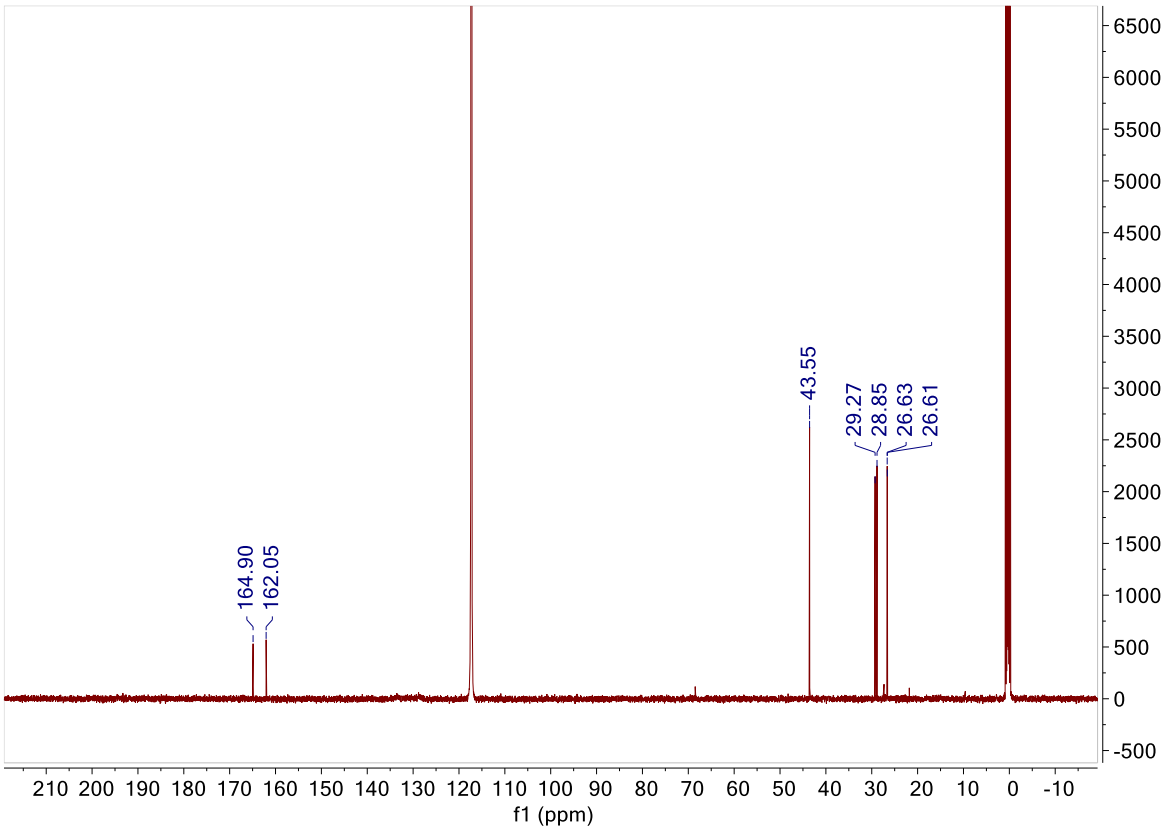
^{1}H and ^{13}C NMR data for 5gg.

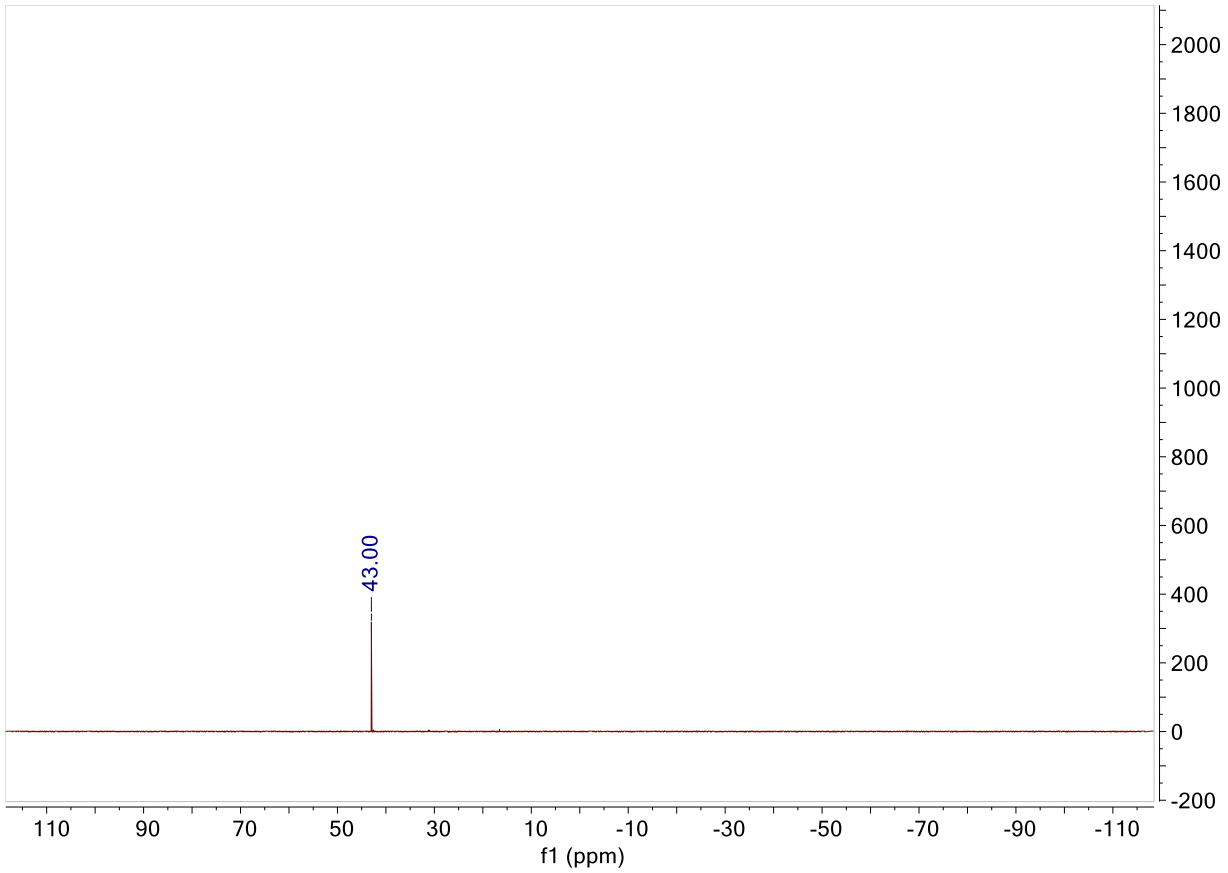




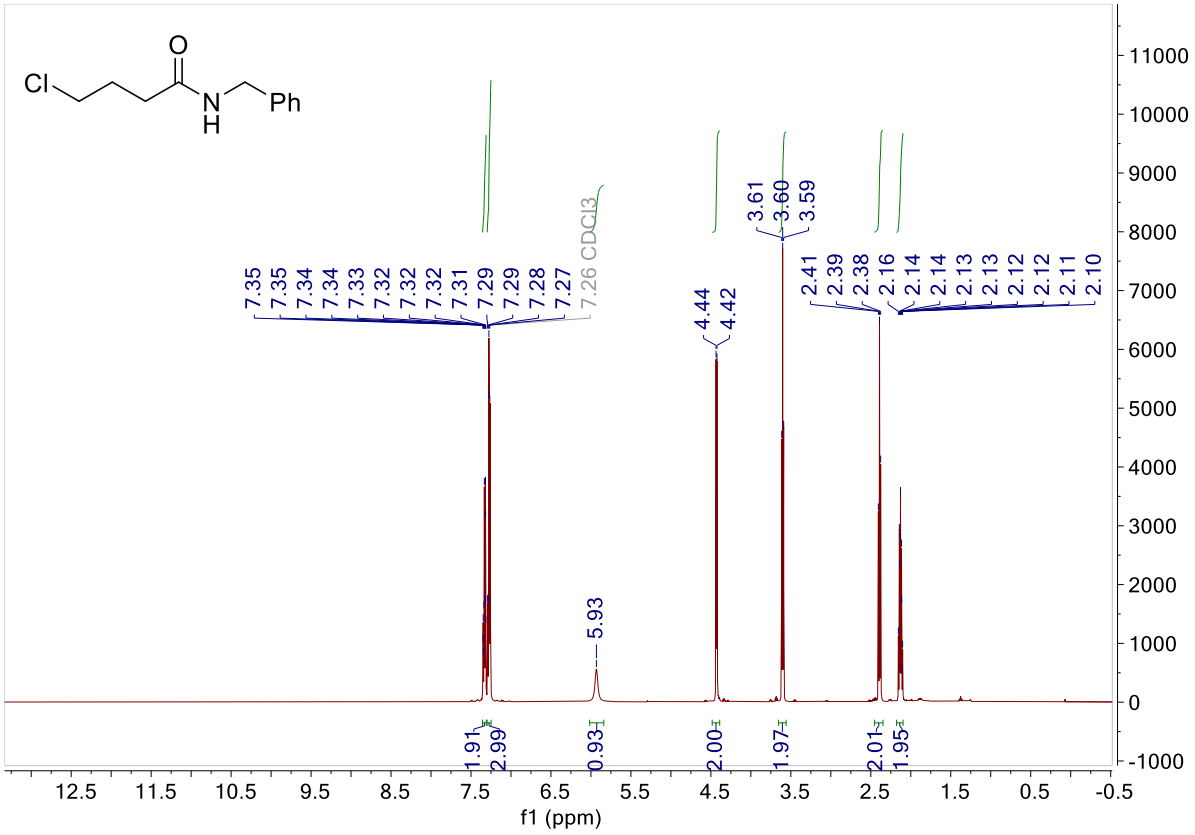
***In situ* ^{1}H, ^{13}C, and ^{19}F NMR data for 1hh.**

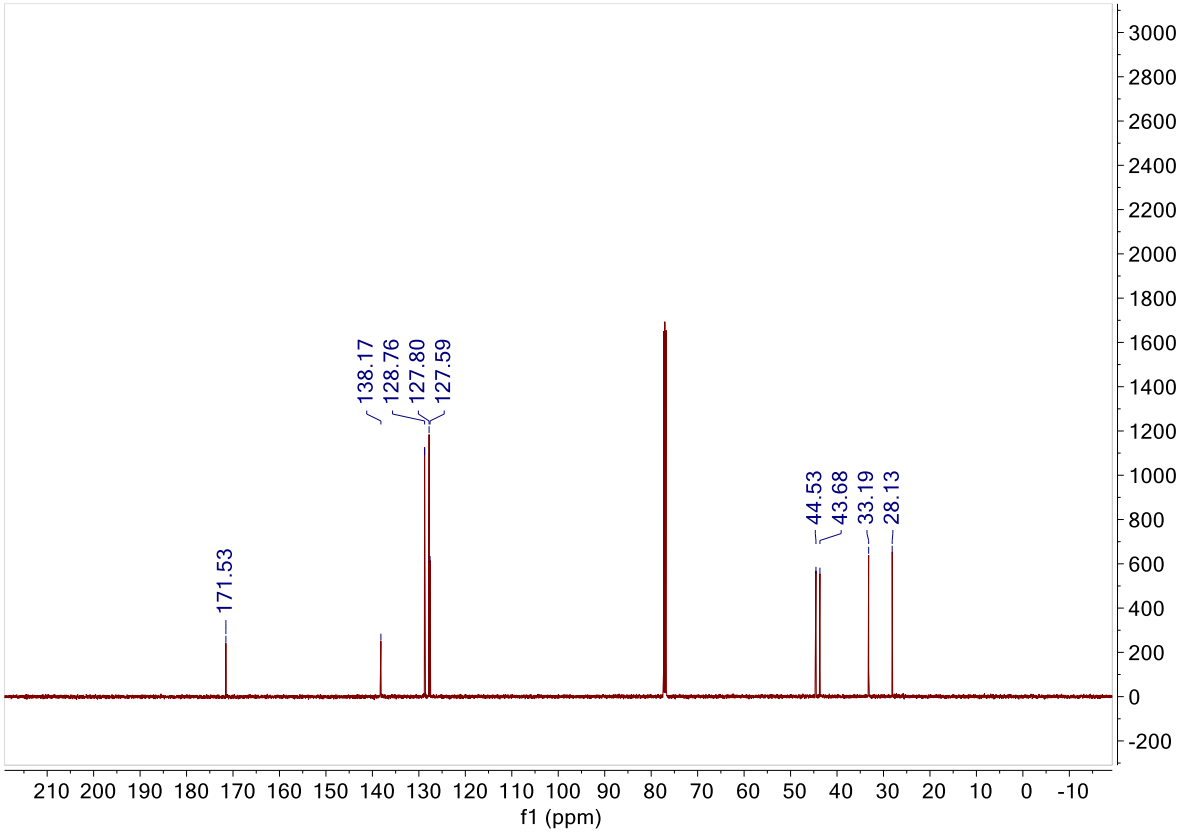




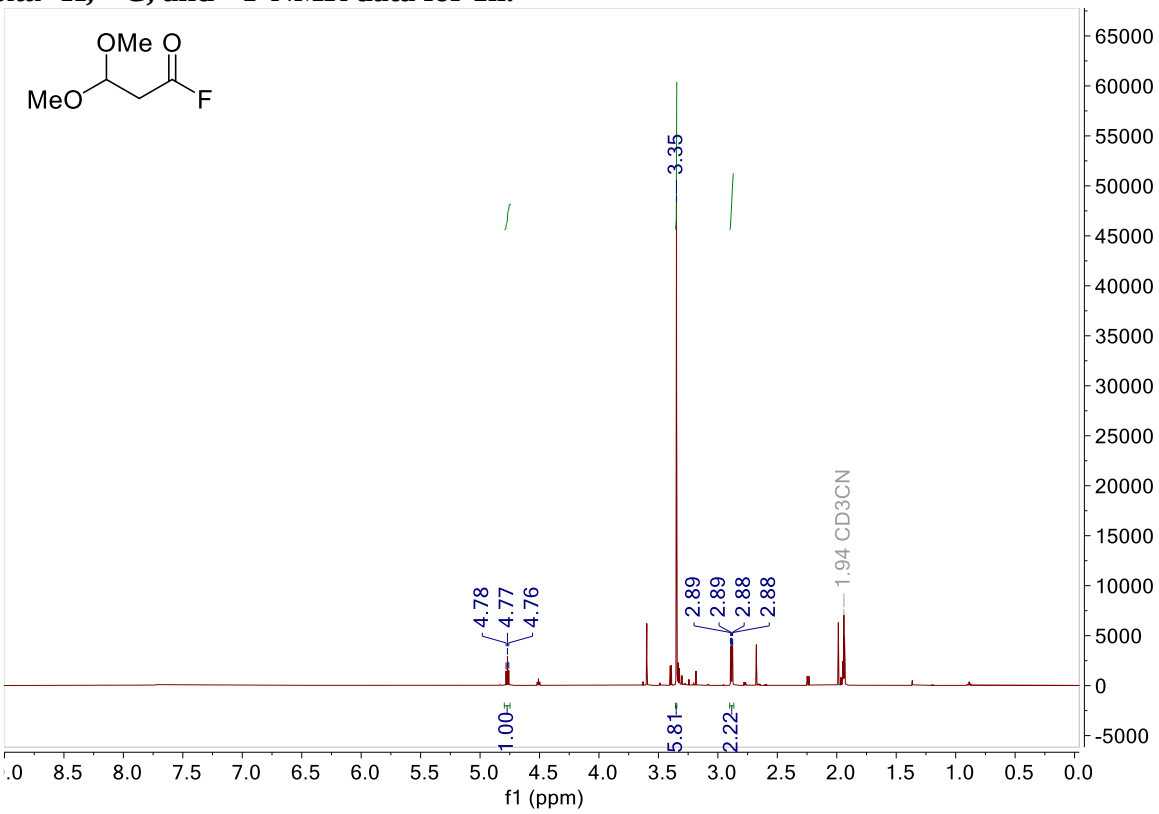

43.00
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
110
90
70
50
30
10
-10
-30
-50
-70
-90
-110
f1 (ppm)

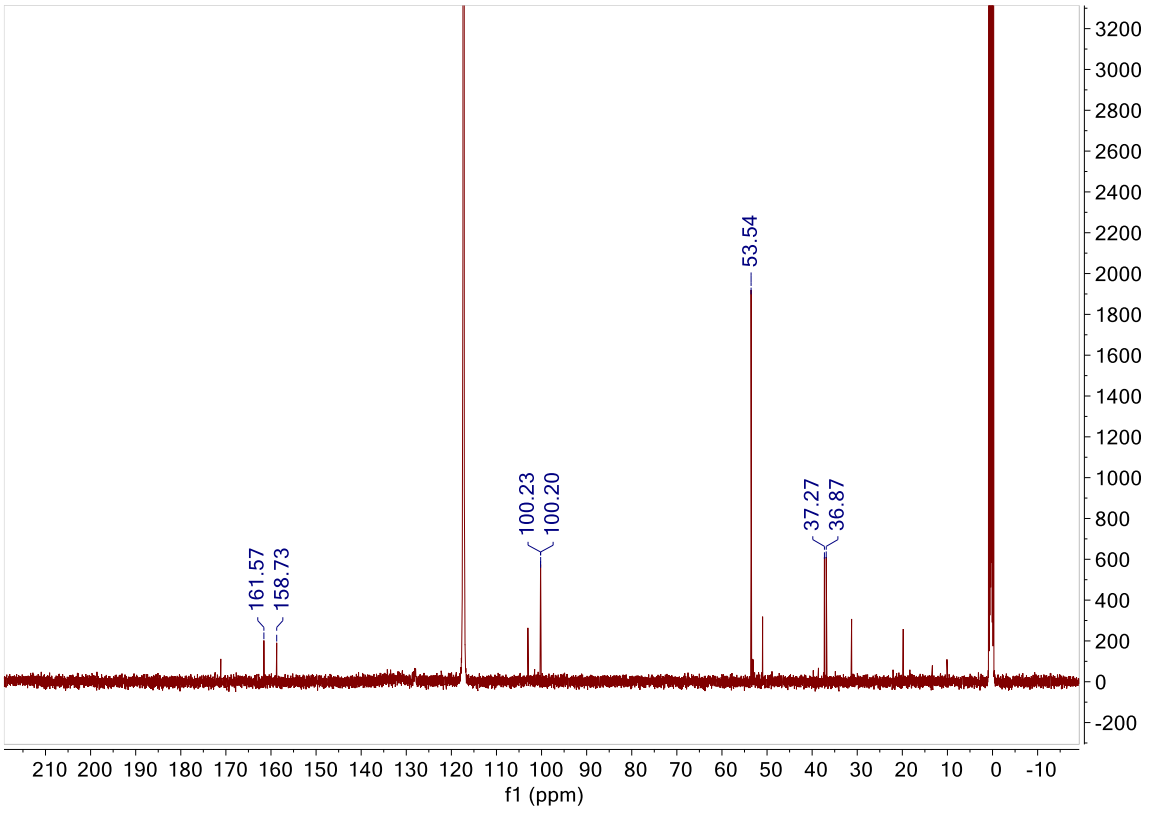
^{1}H and ^{13}C NMR data for 5hh.

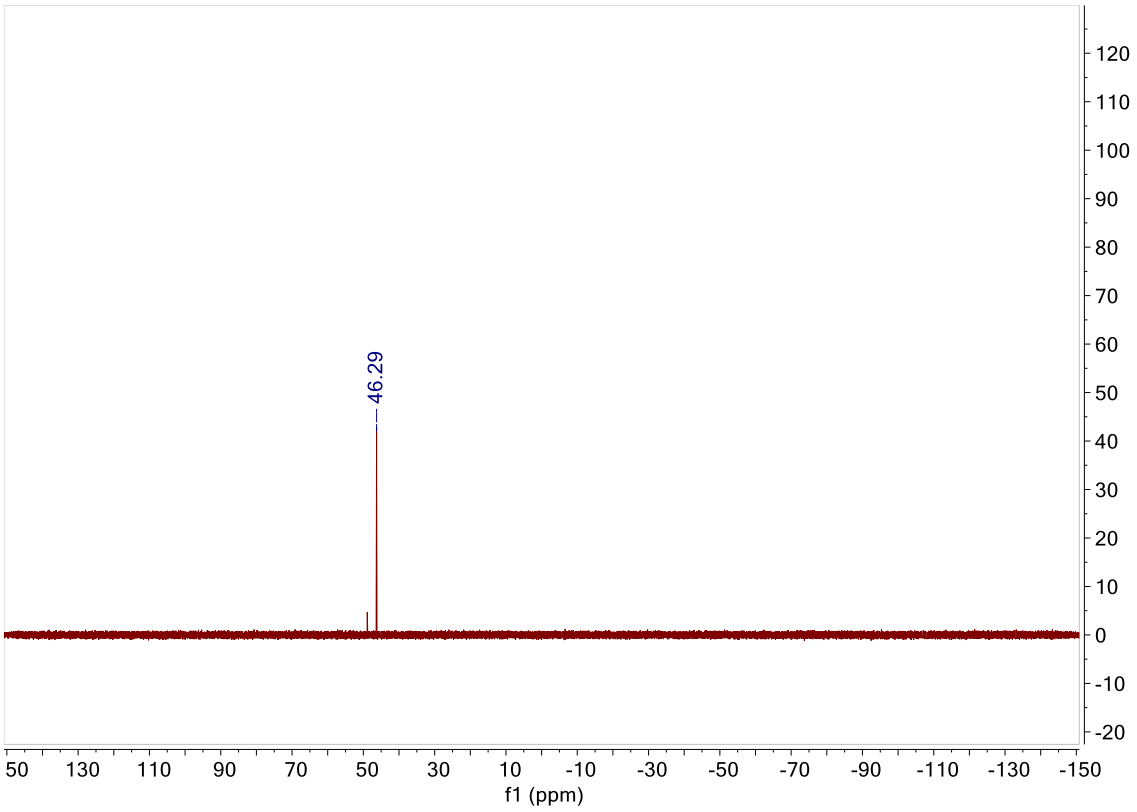




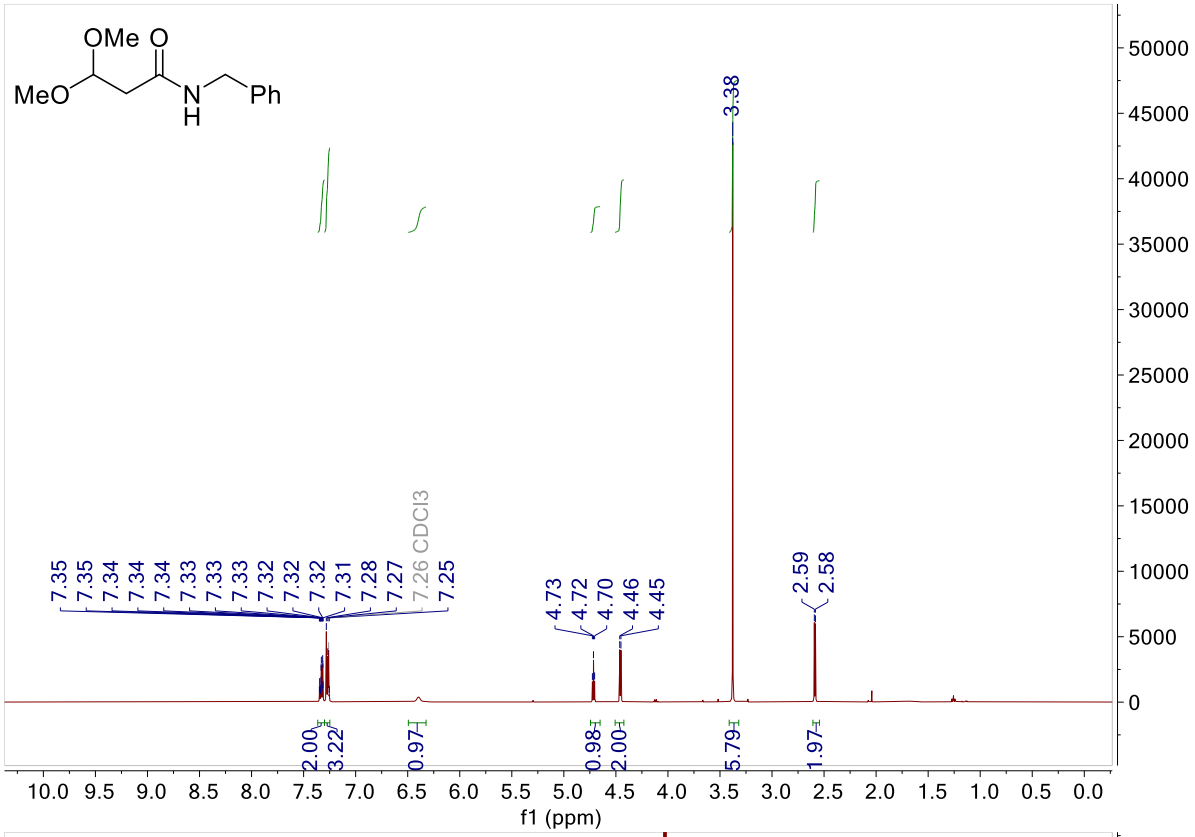
***In situ* ^{1}H, ^{13}C, and ^{19}F NMR data for 1ii.**

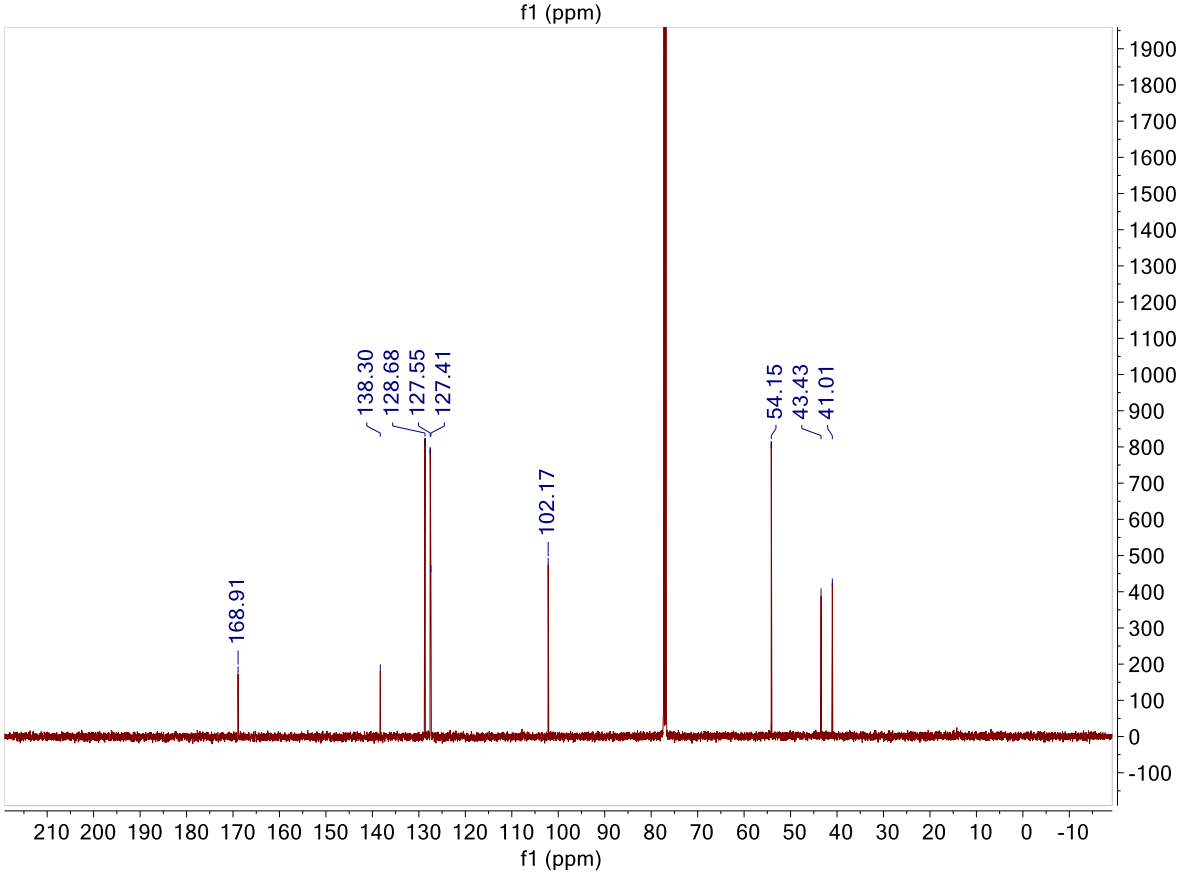




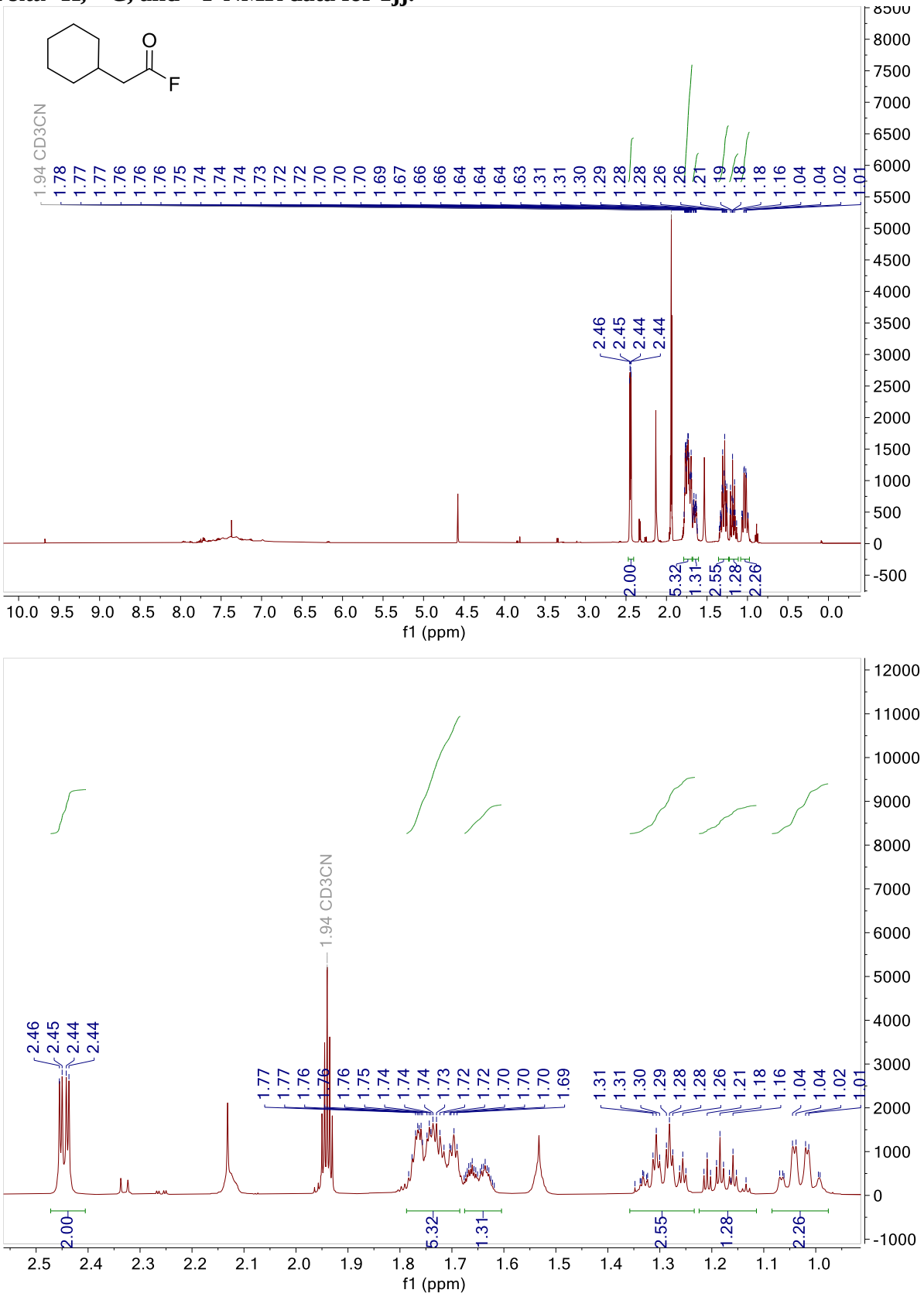

46.29
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
50
130
110
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
f1 (ppm)

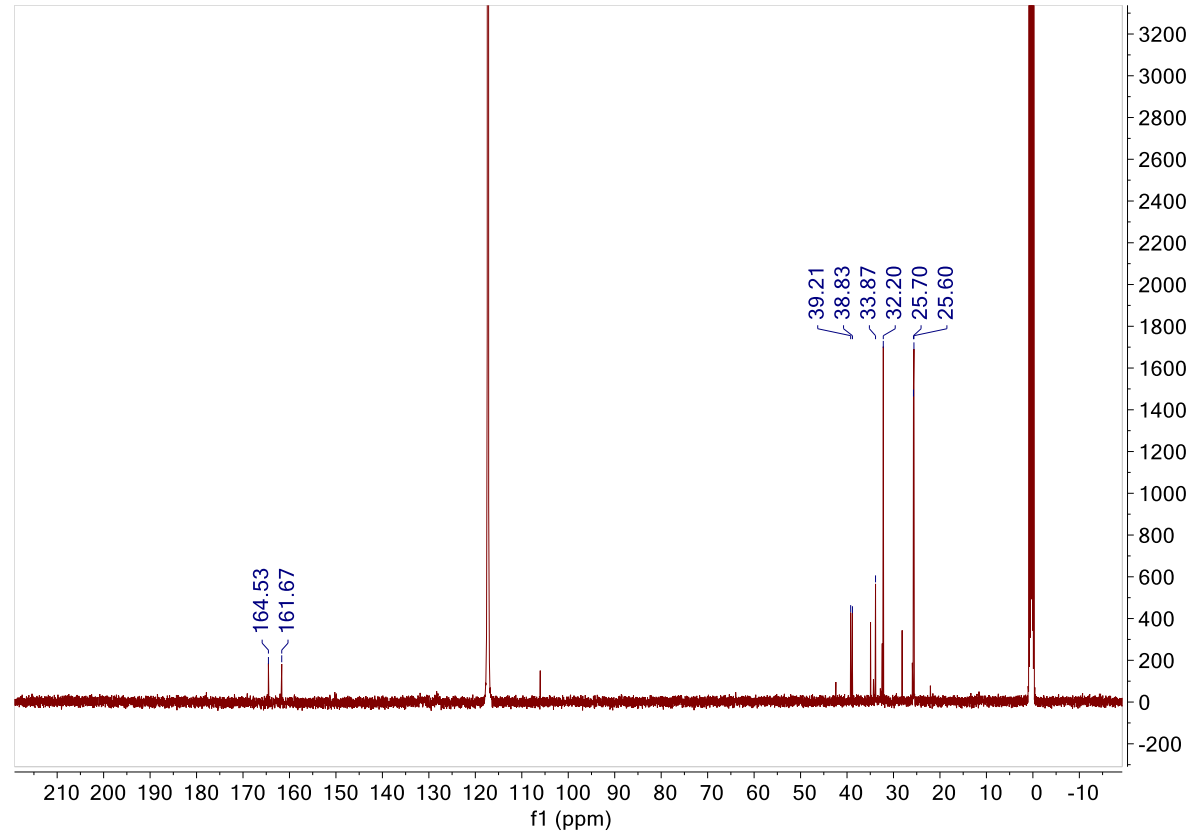
^{1}H and ^{13}C NMR data for 5ii.

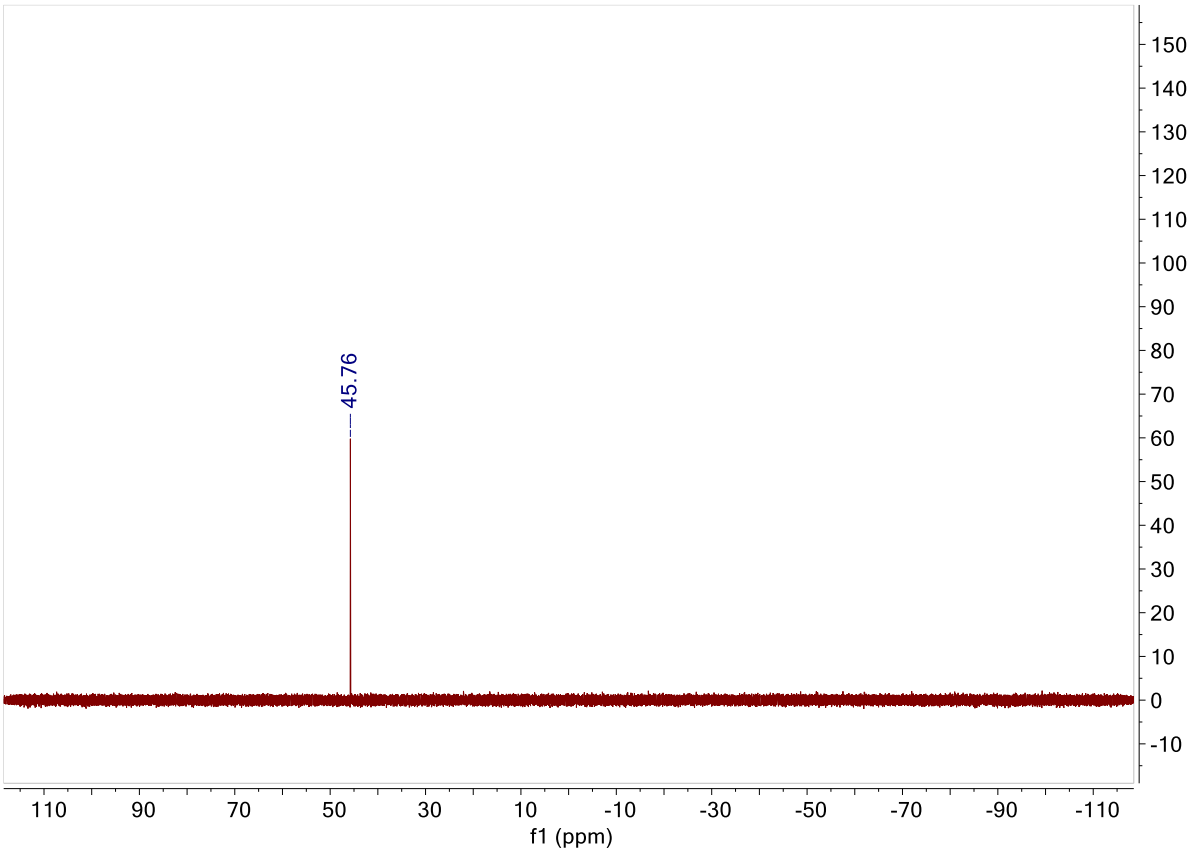




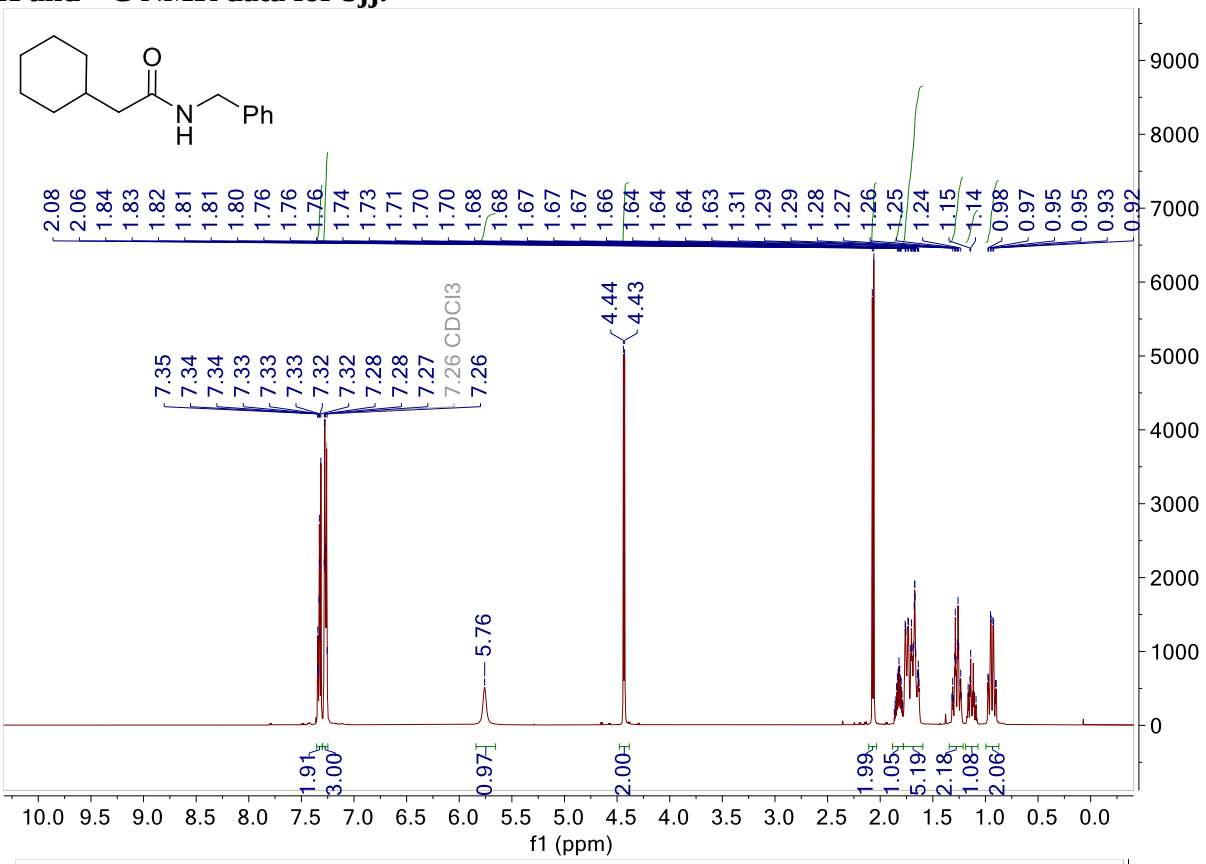
***In situ* ^{1}H, ^{13}C, and ^{19}F NMR data for 1jj.**

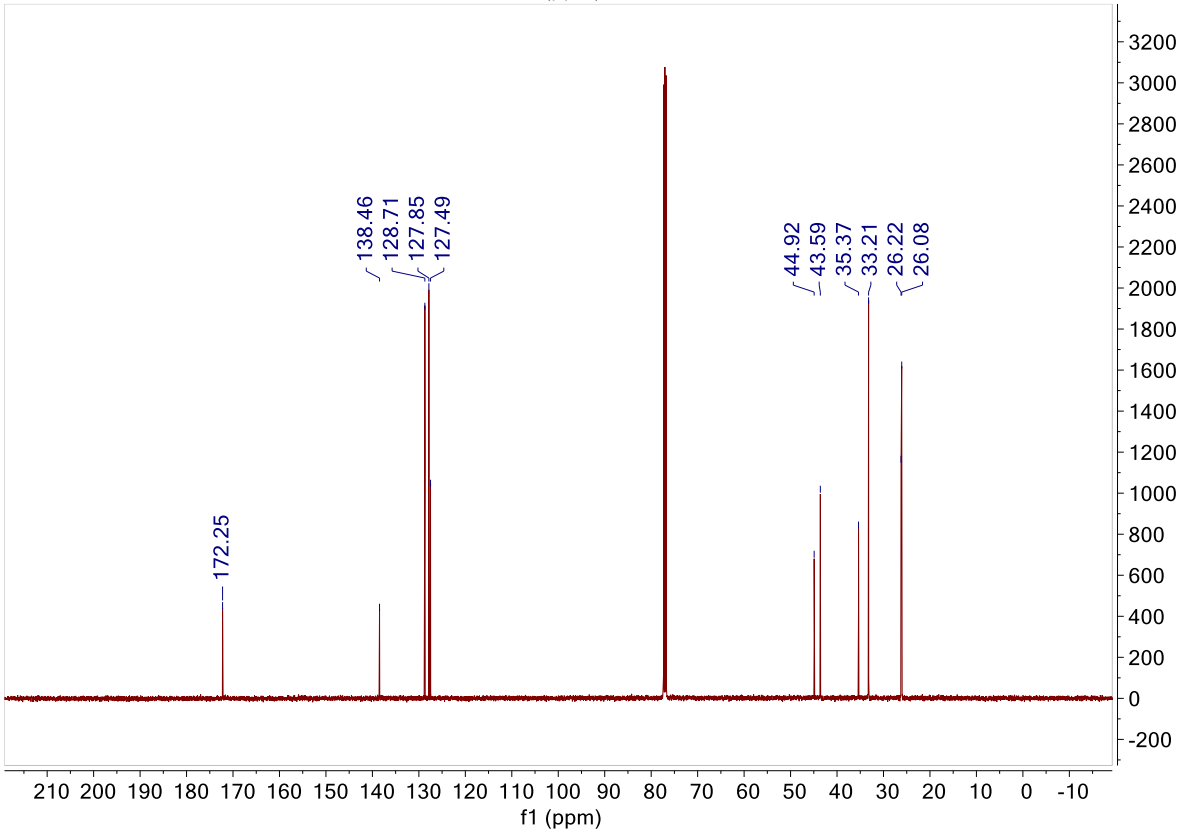



164.53
161.67
39.21
38.83
33.87
32.20
25.70
25.60
f1 (ppm)

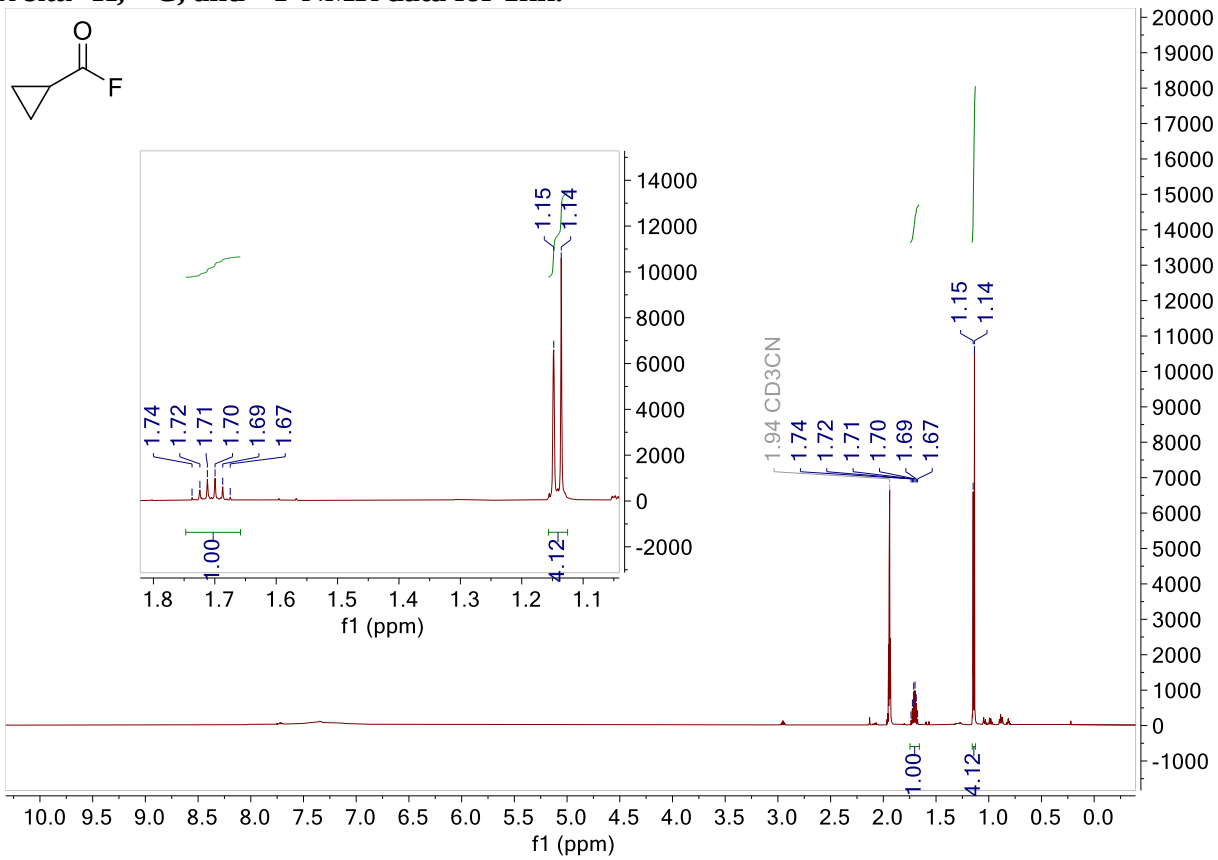

45.76
f1 (ppm)

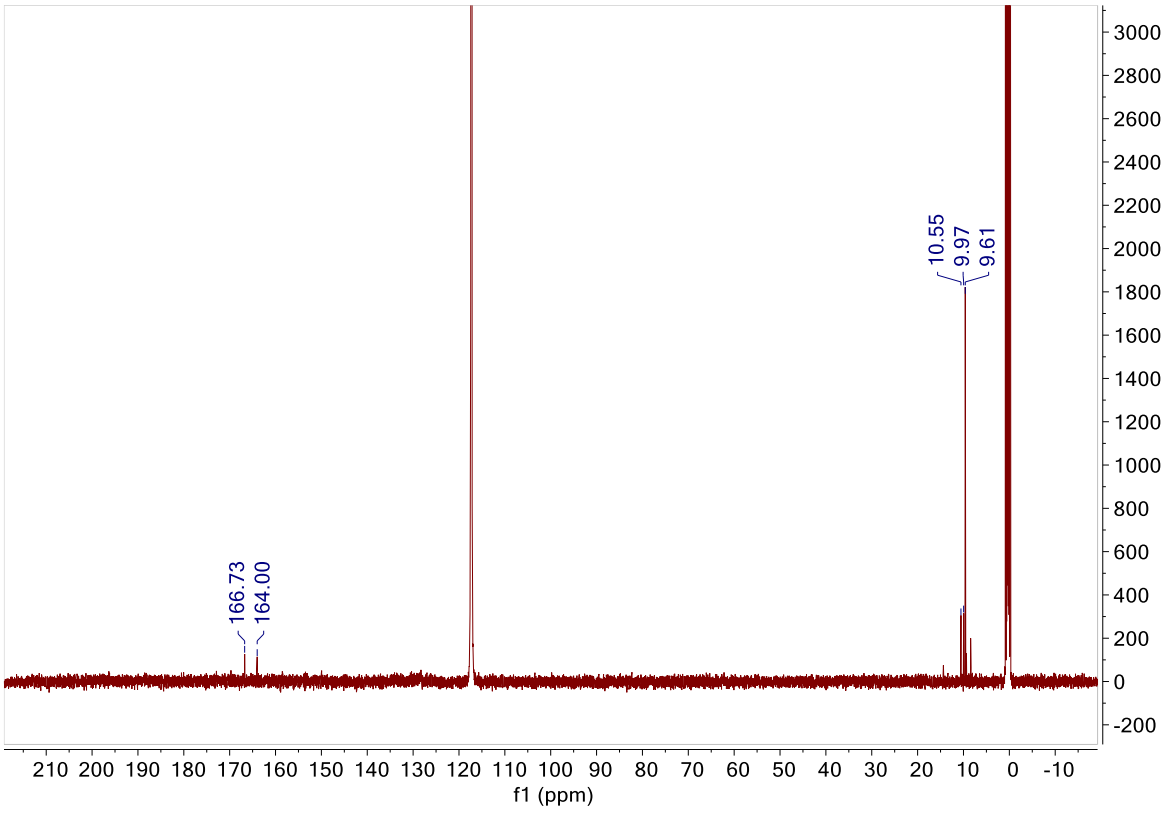
^{1}H and ^{13}C NMR data for 5jj.

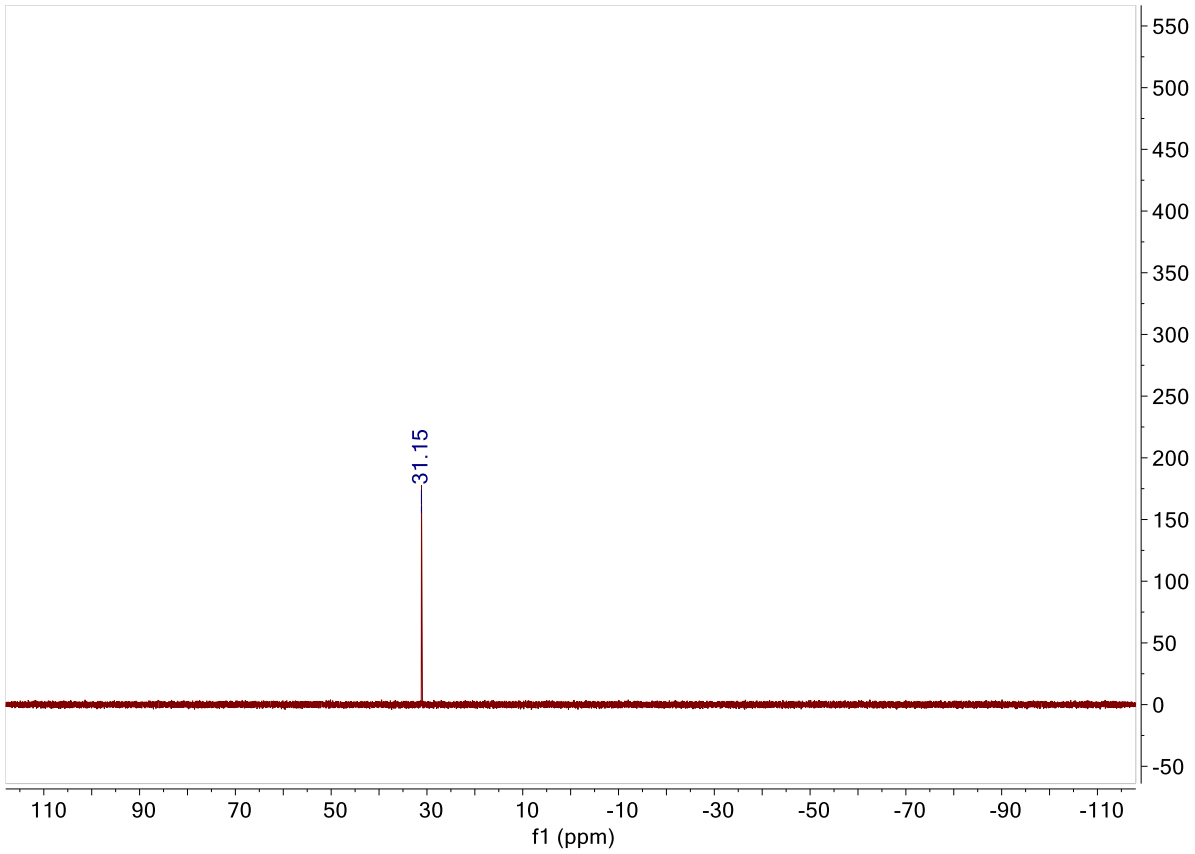




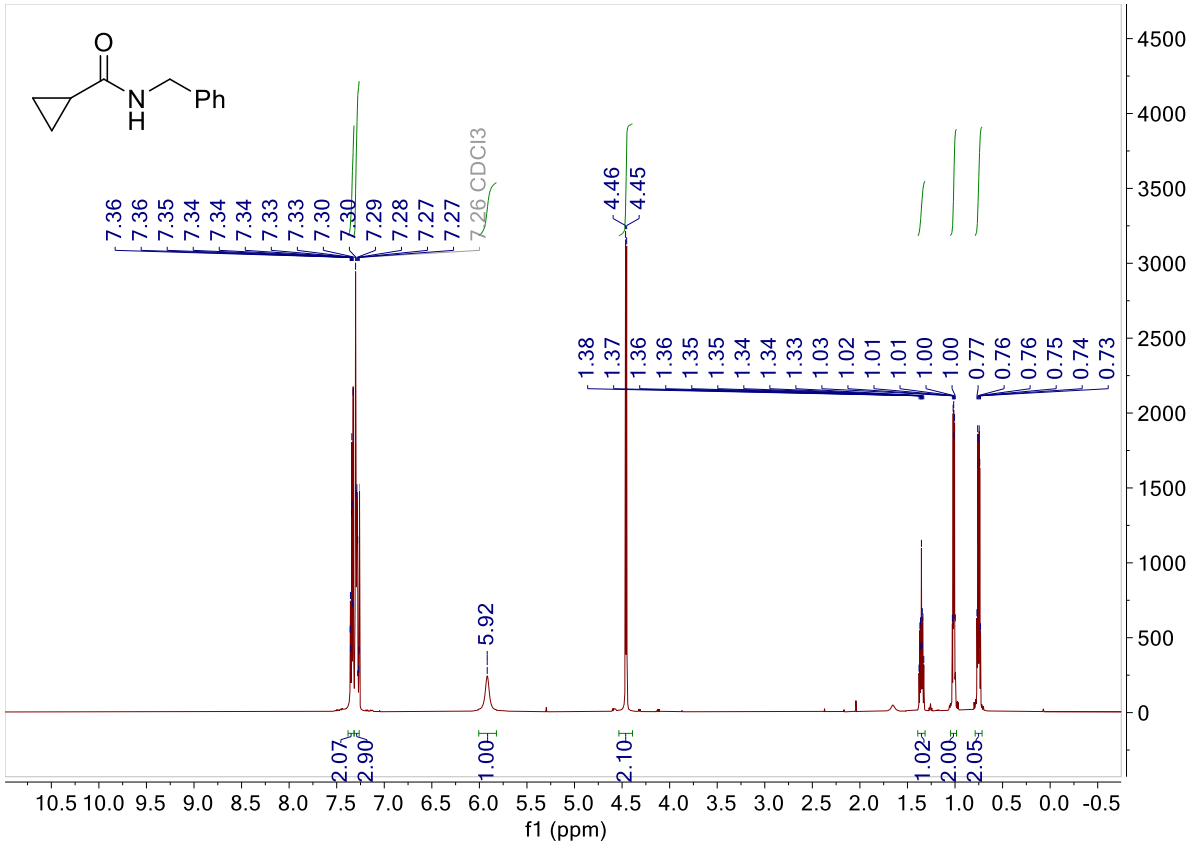
***In situ* ^{1}H, ^{13}C, and ^{19}F NMR data for 1kk.**

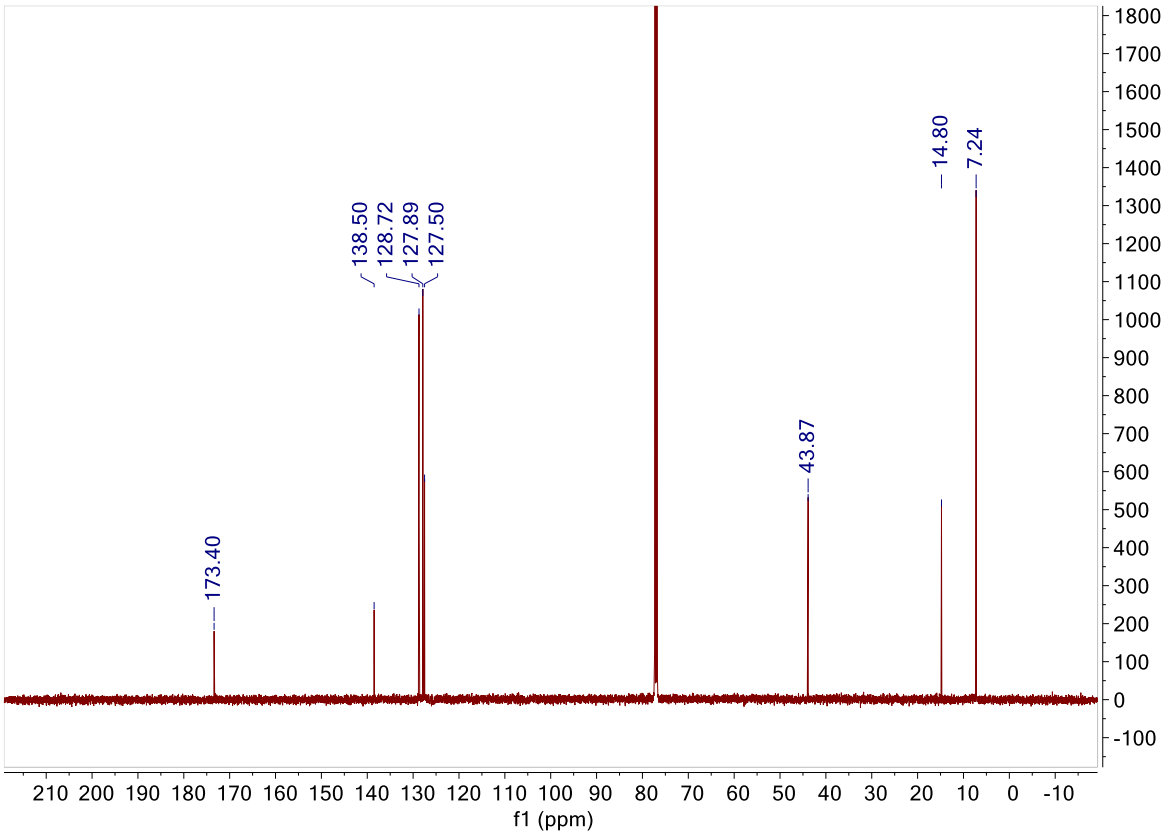




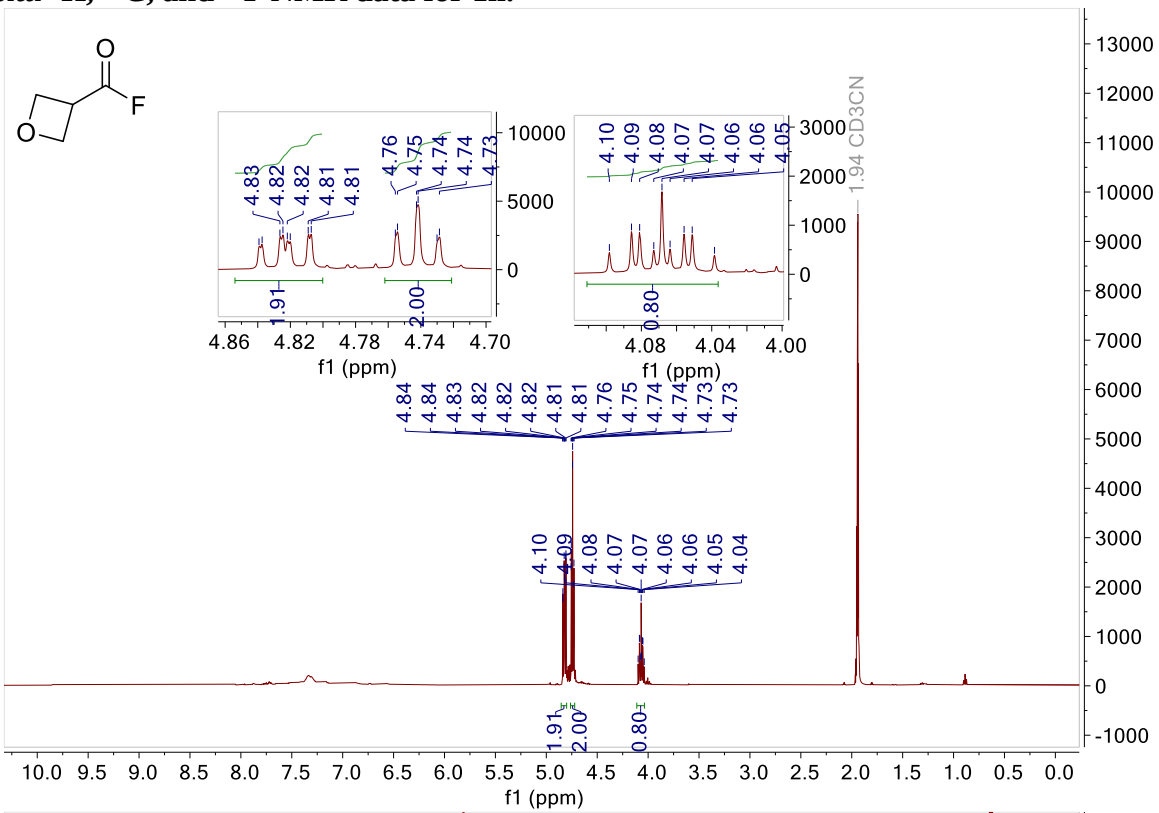

31.15
550
500
450
400
350
300
250
200
150
100
50
0
-50
110
90
70
50
30
10
-10
-30
-50
-70
-90
-110
f1 (ppm)

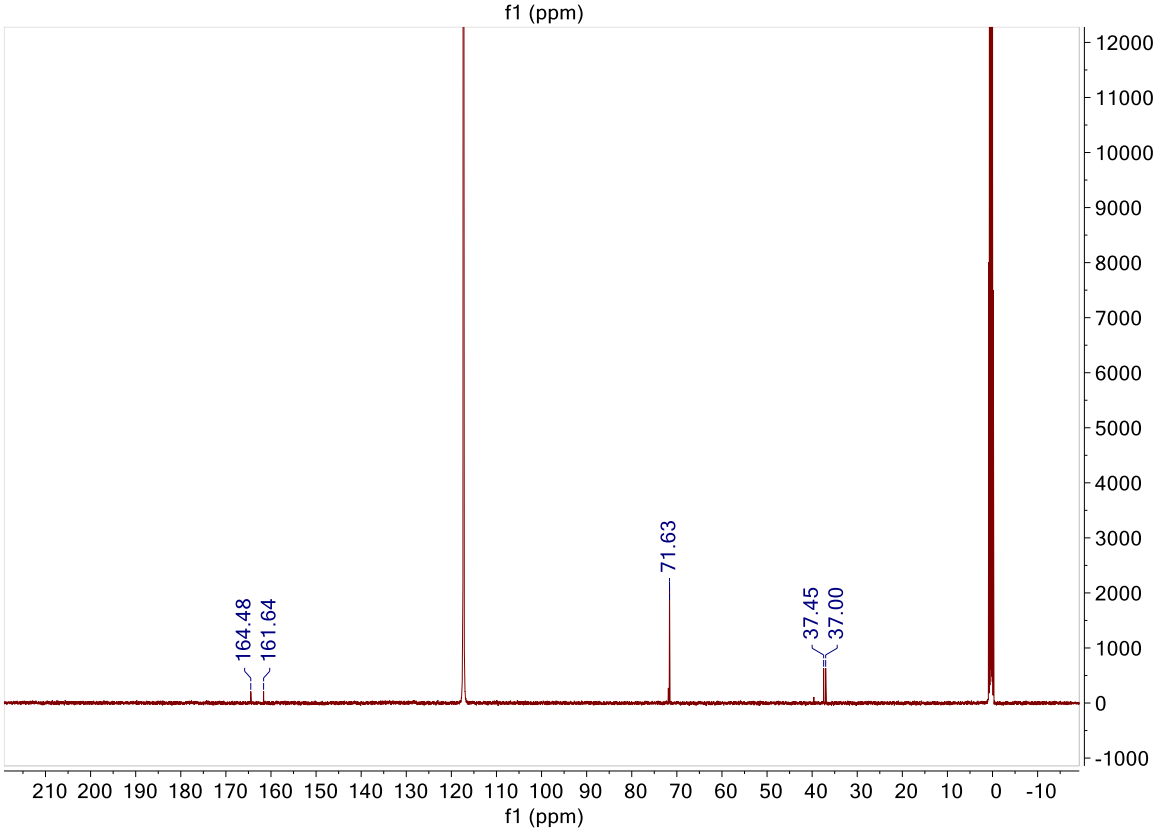
^{1}H and ^{13}C NMR data for 5kk.

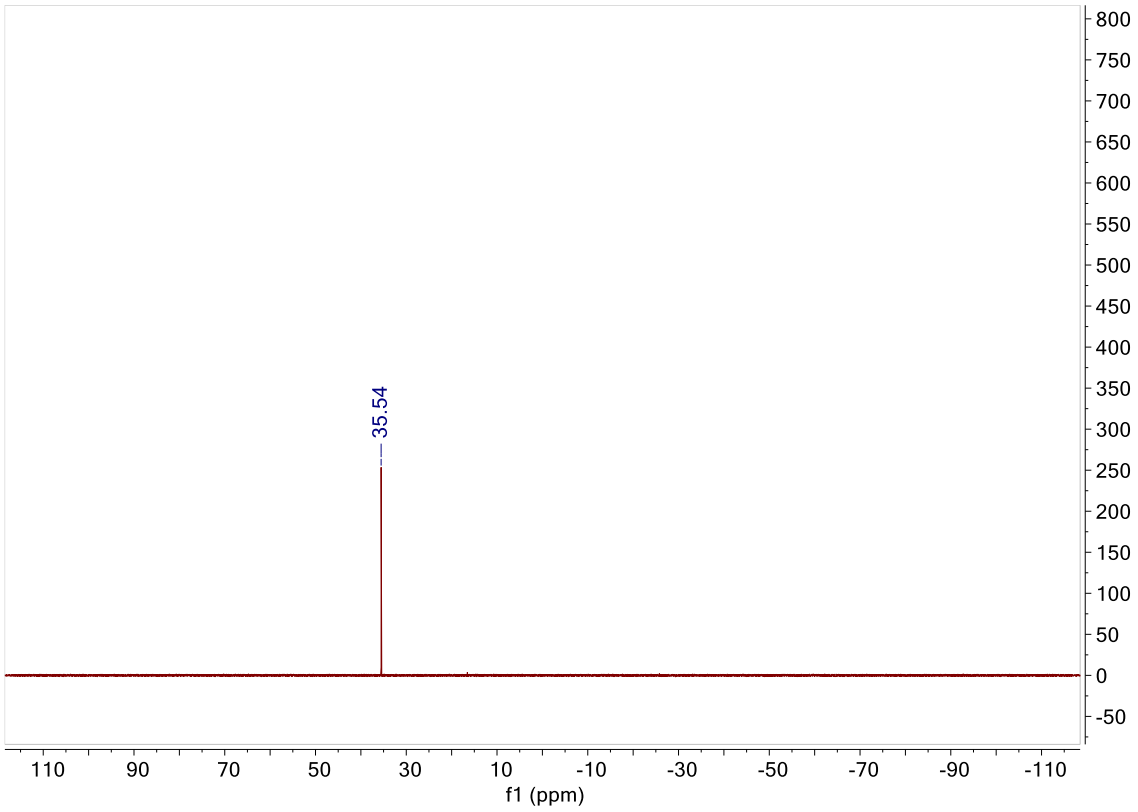




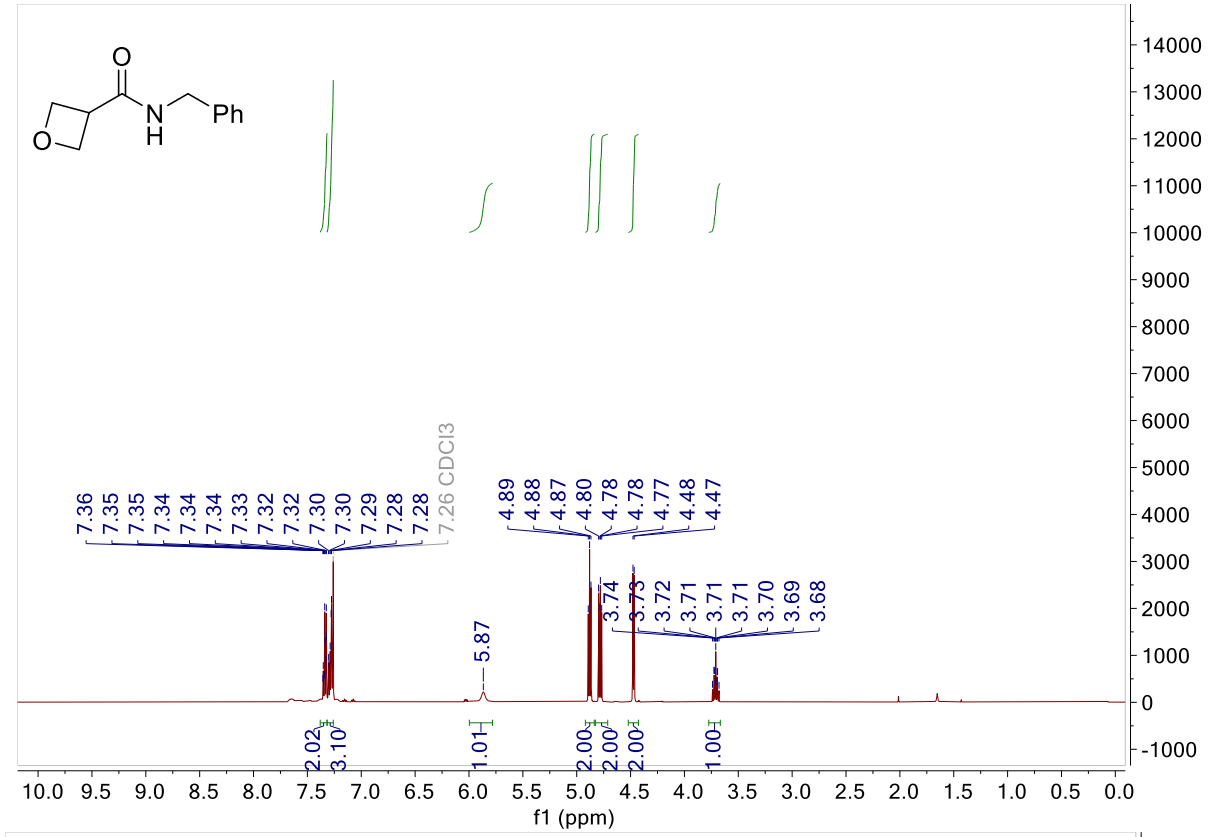
***In situ* ^{1}H, ^{13}C, and ^{19}F NMR data for 1ll.**

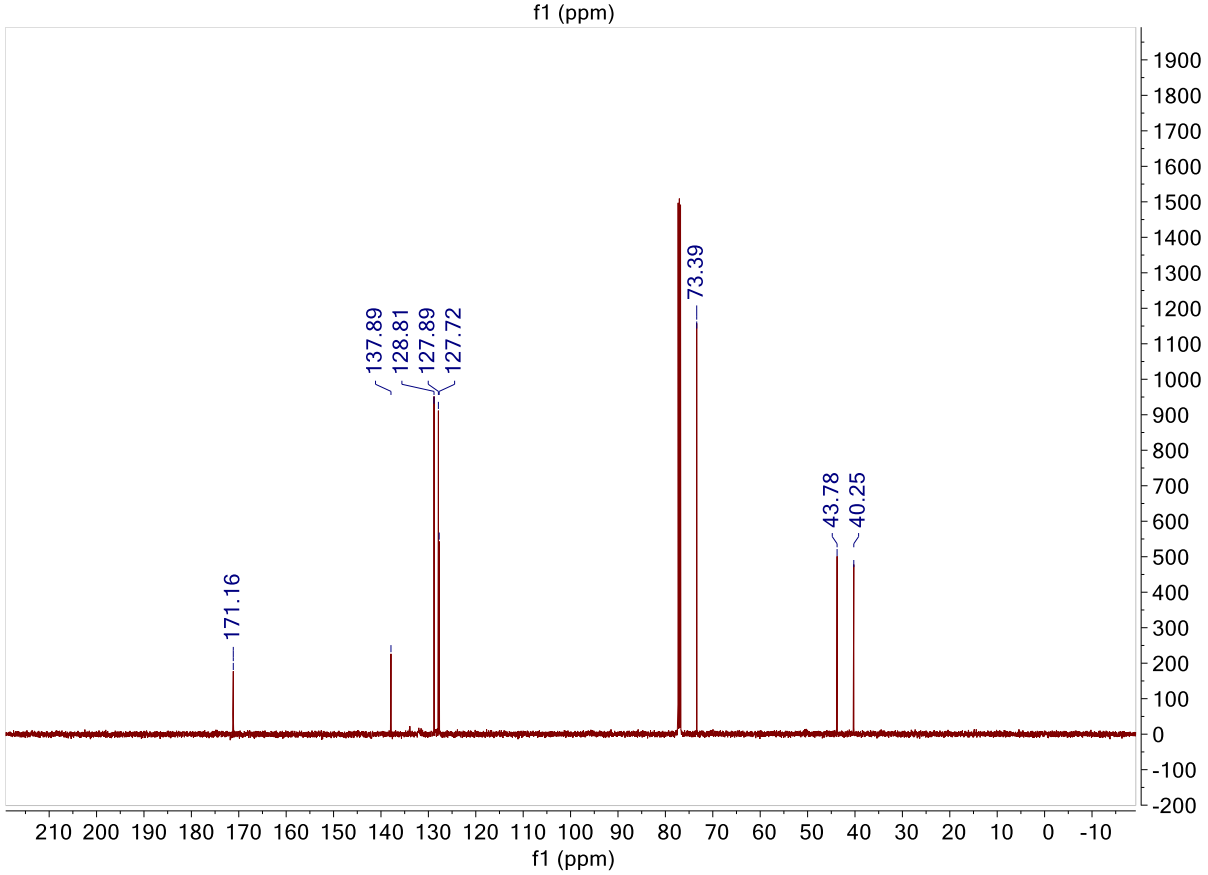




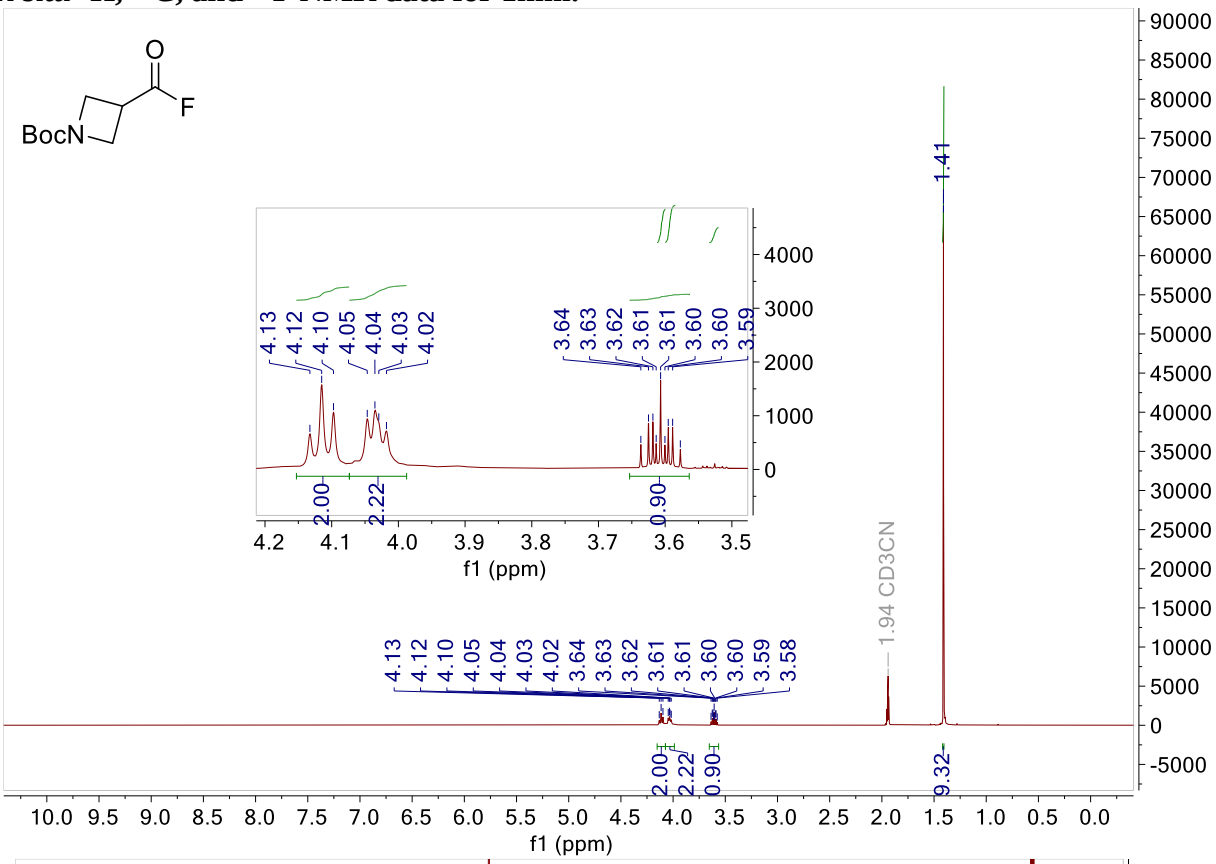

35.54
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
110
90
70
50
30
10
-10
-30
-50
-70
-90
-110
f1 (ppm)

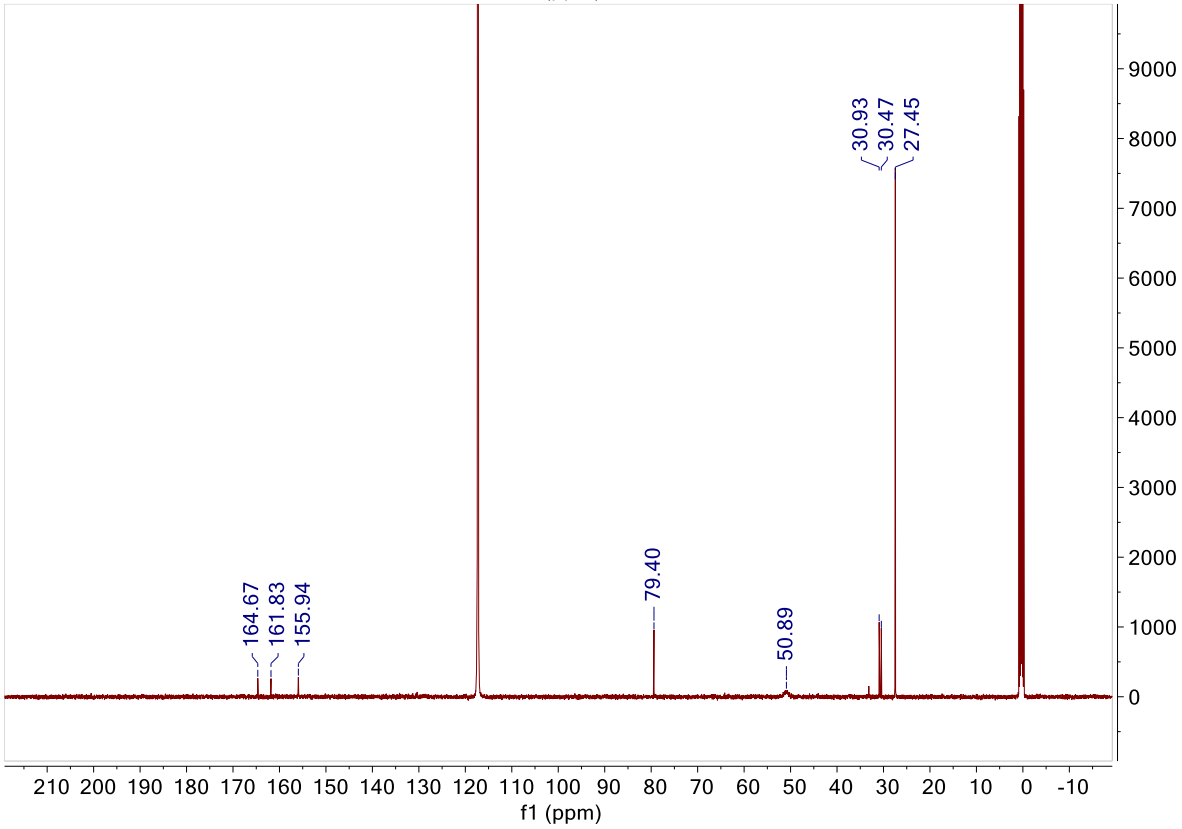
^{1}H and ^{13}C NMR data for 5ll.

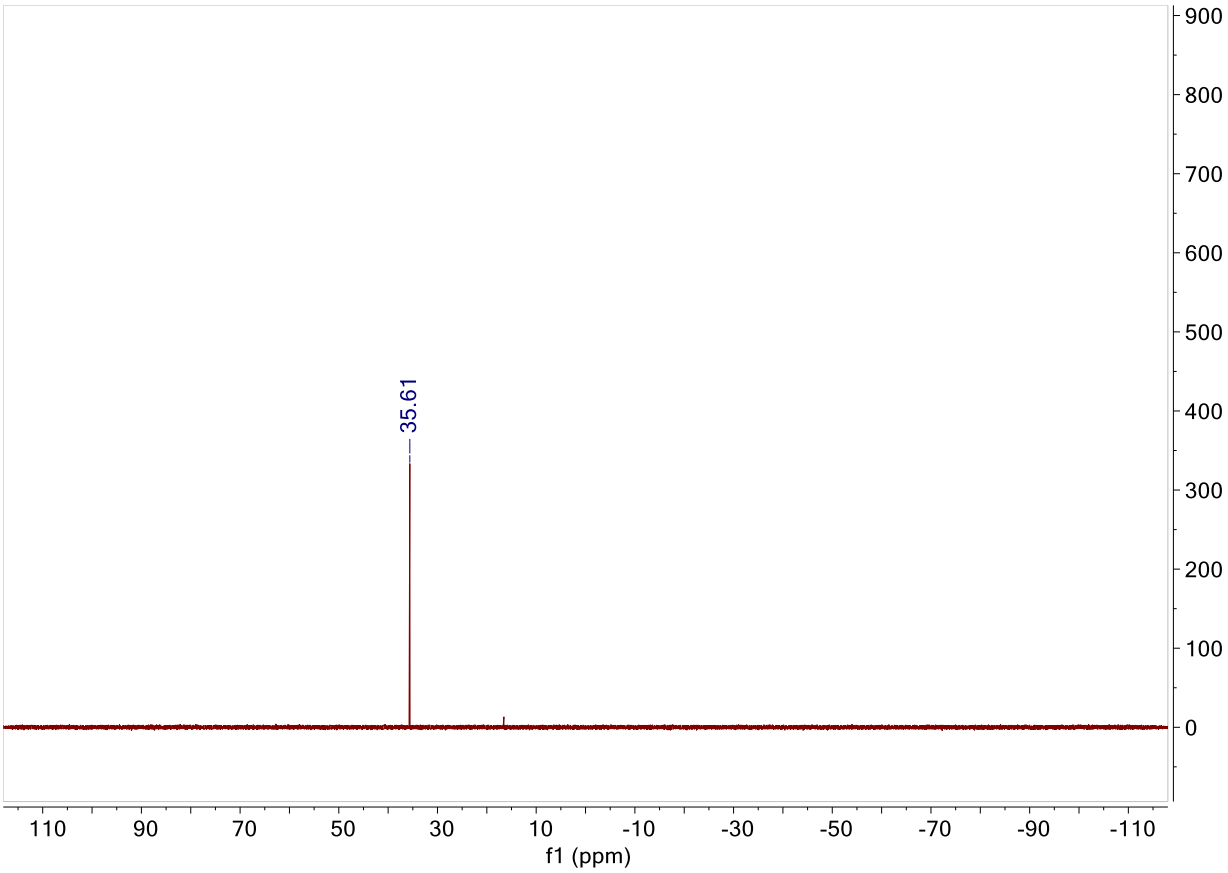




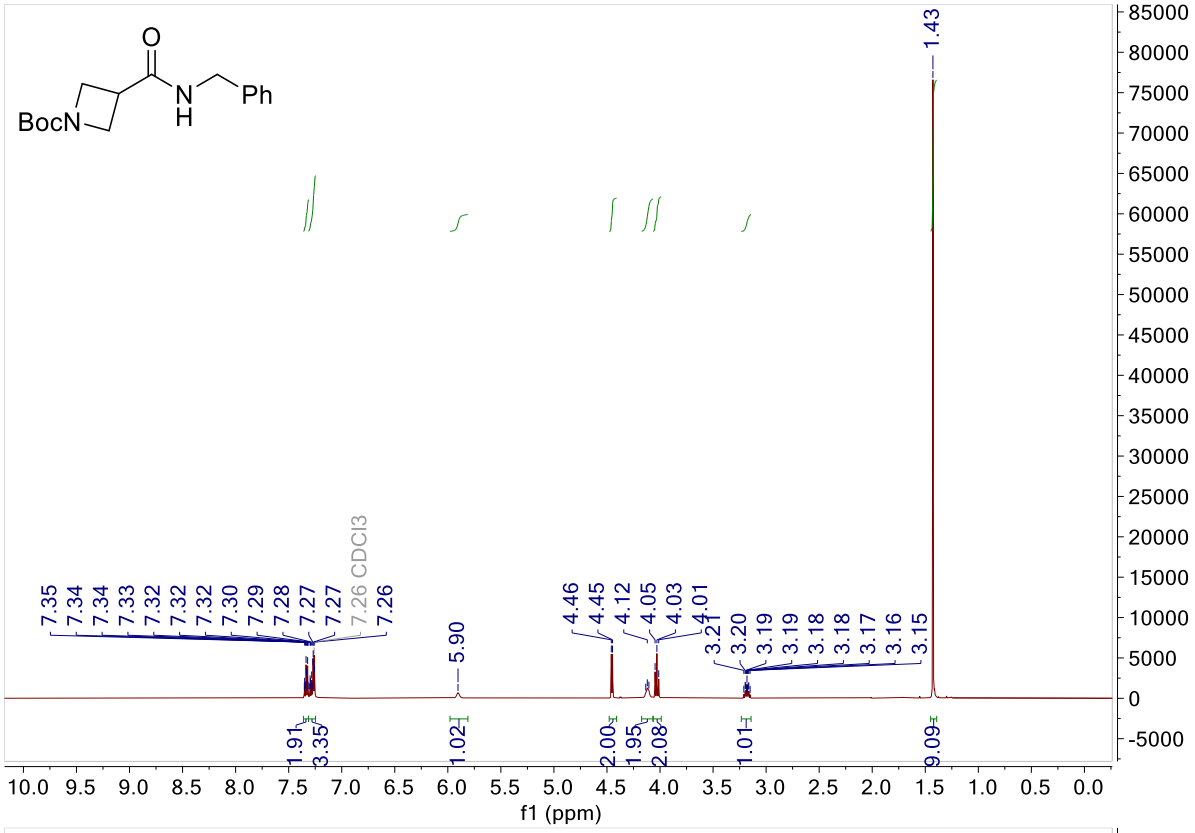
***In situ* ^{1}H, ^{13}C, and ^{19}F NMR data for 1mm.**

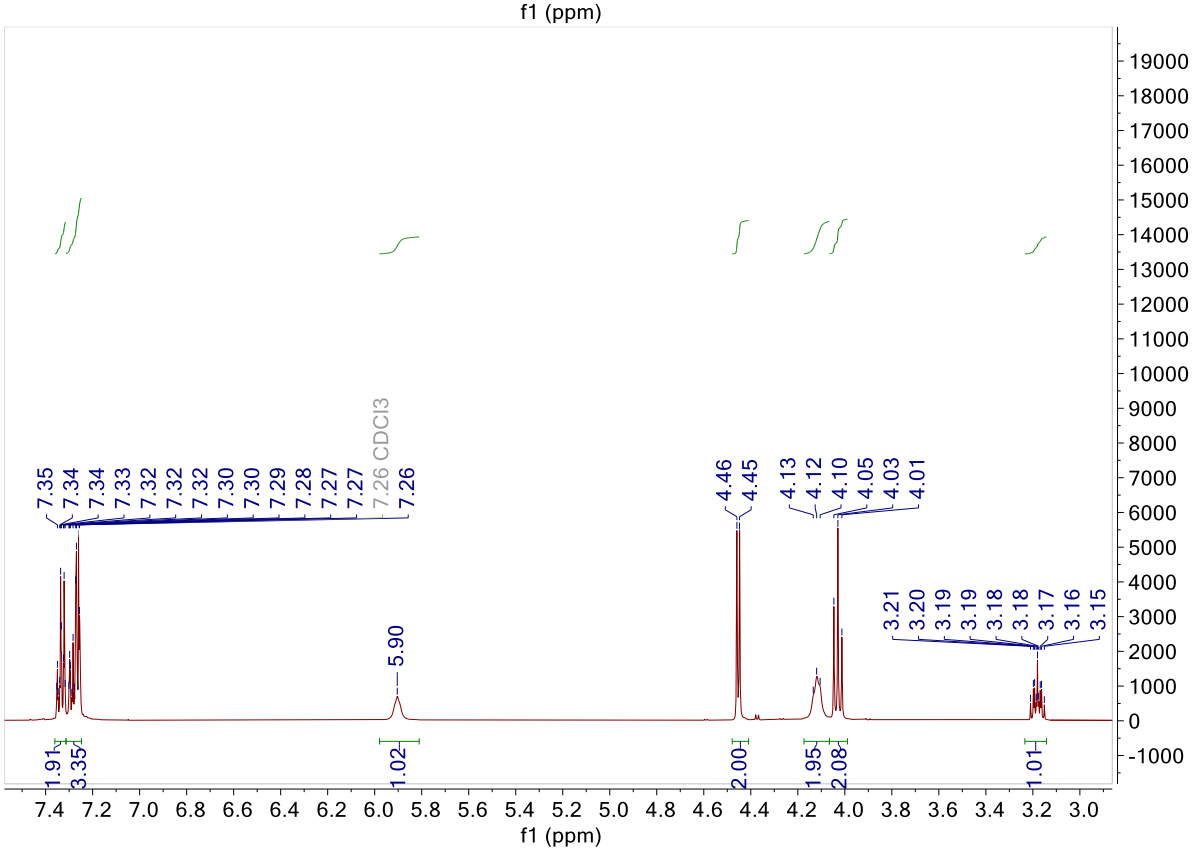


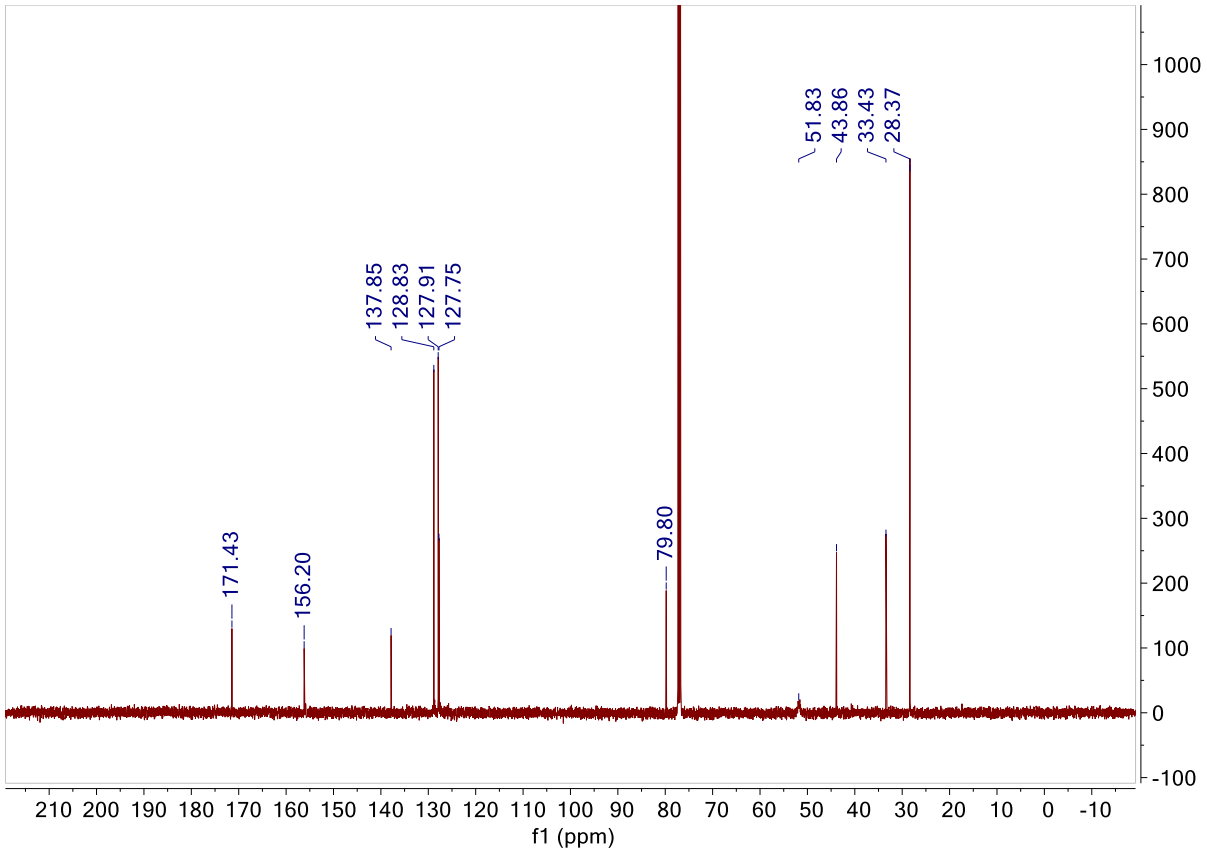



35.61
900
800
700
600
500
400
300
200
100
0
110
90
70
50
30
10
-10
-30
-50
-70
-90
-110
f1 (ppm)

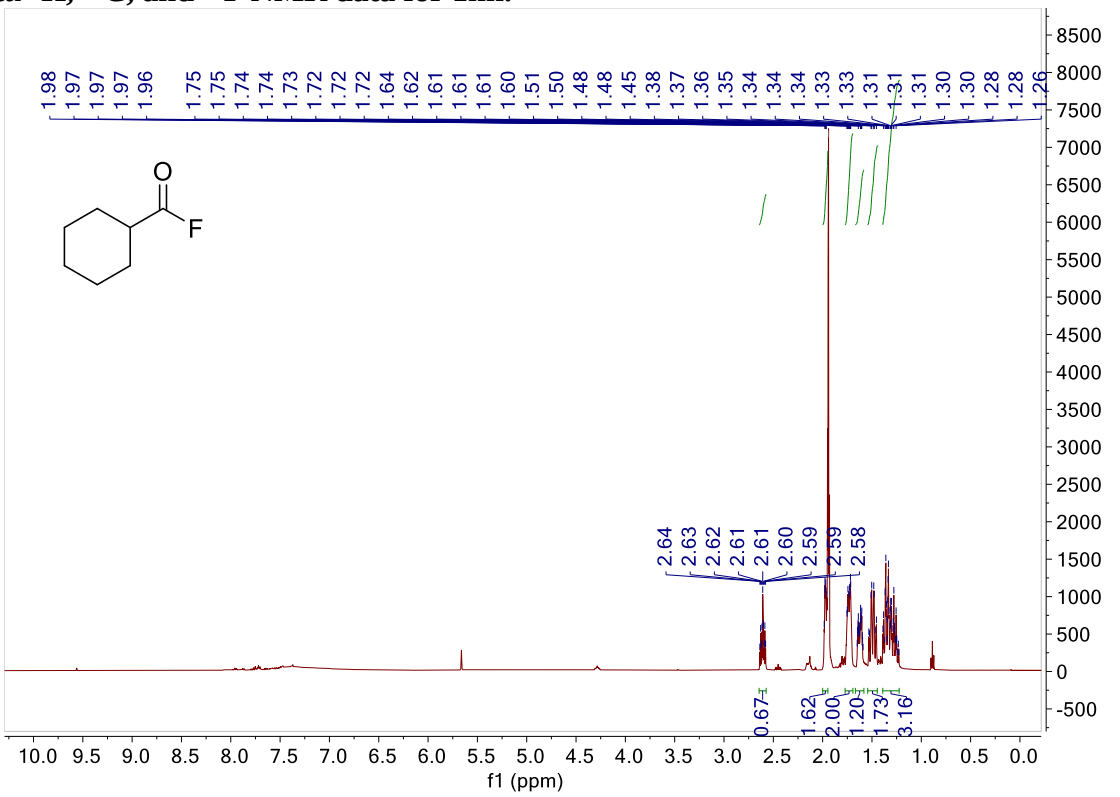
^{1}H and ^{13}C NMR data for 5mm.

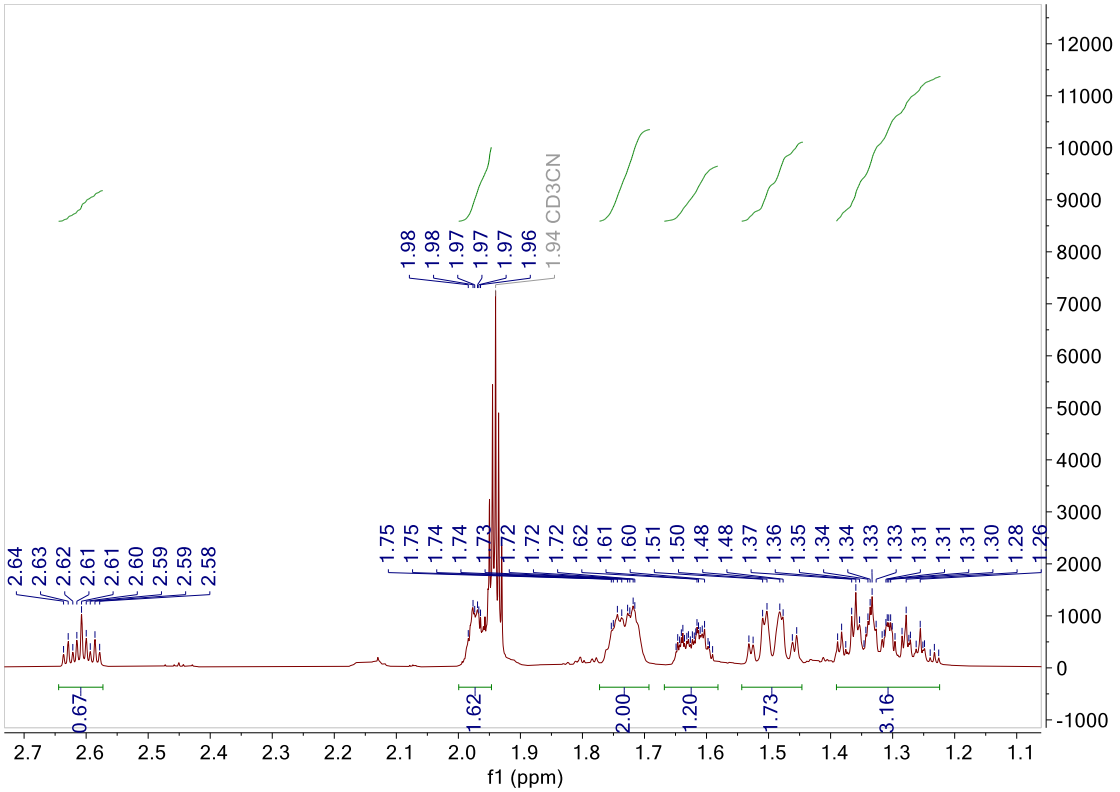


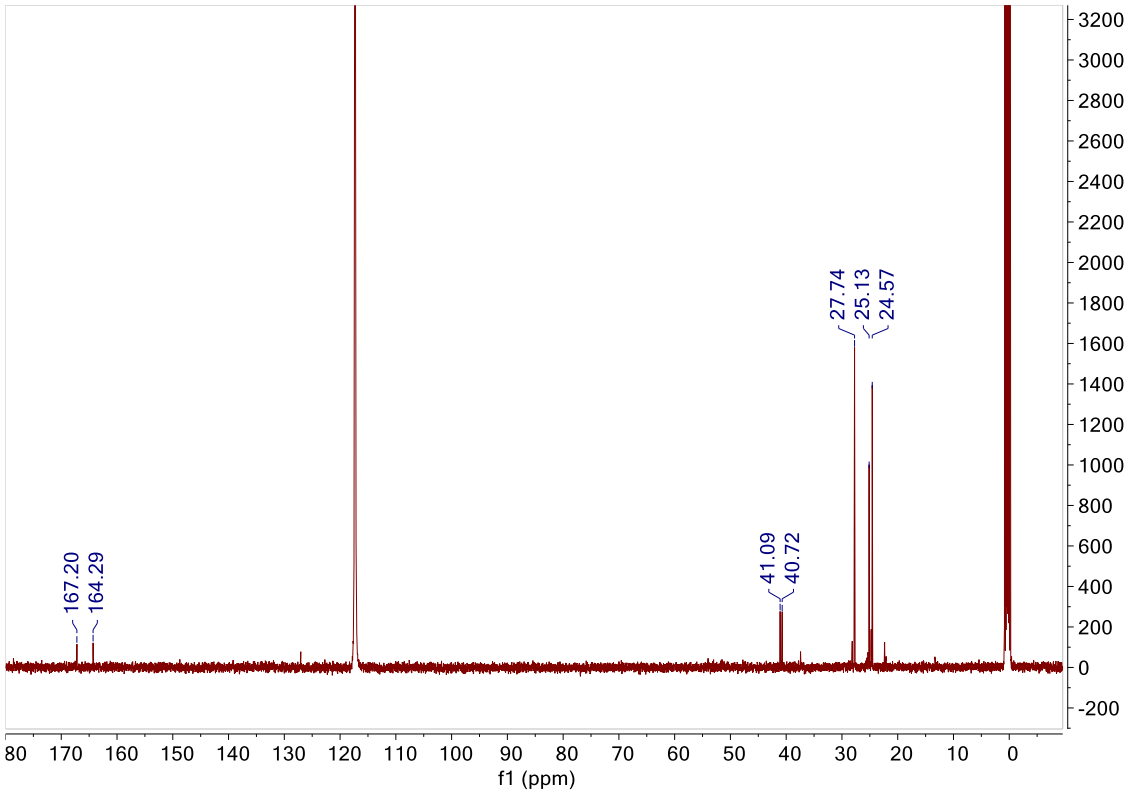


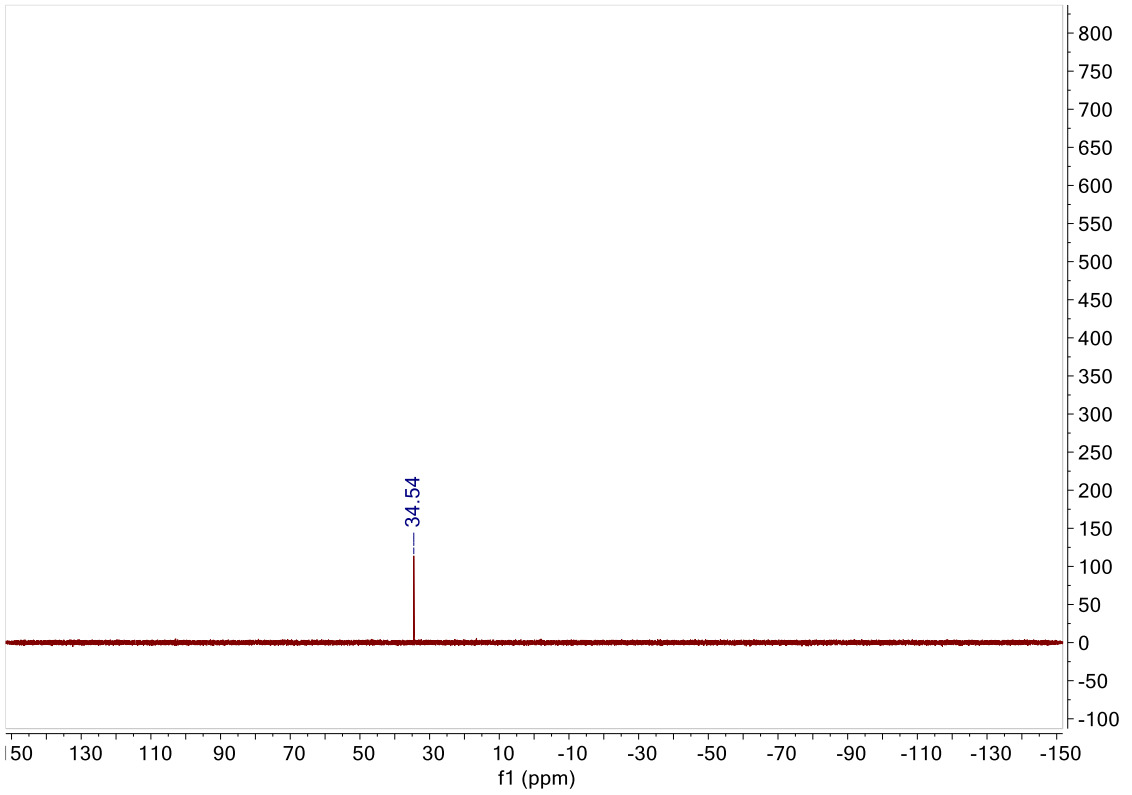

171.43
156.20
137.85
128.83
127.91
127.75
79.80
51.83
43.86
33.43
28.37
f1 (ppm)

***In situ* ^{1}H, ^{13}C, and ^{19}F NMR data for 1nn.**

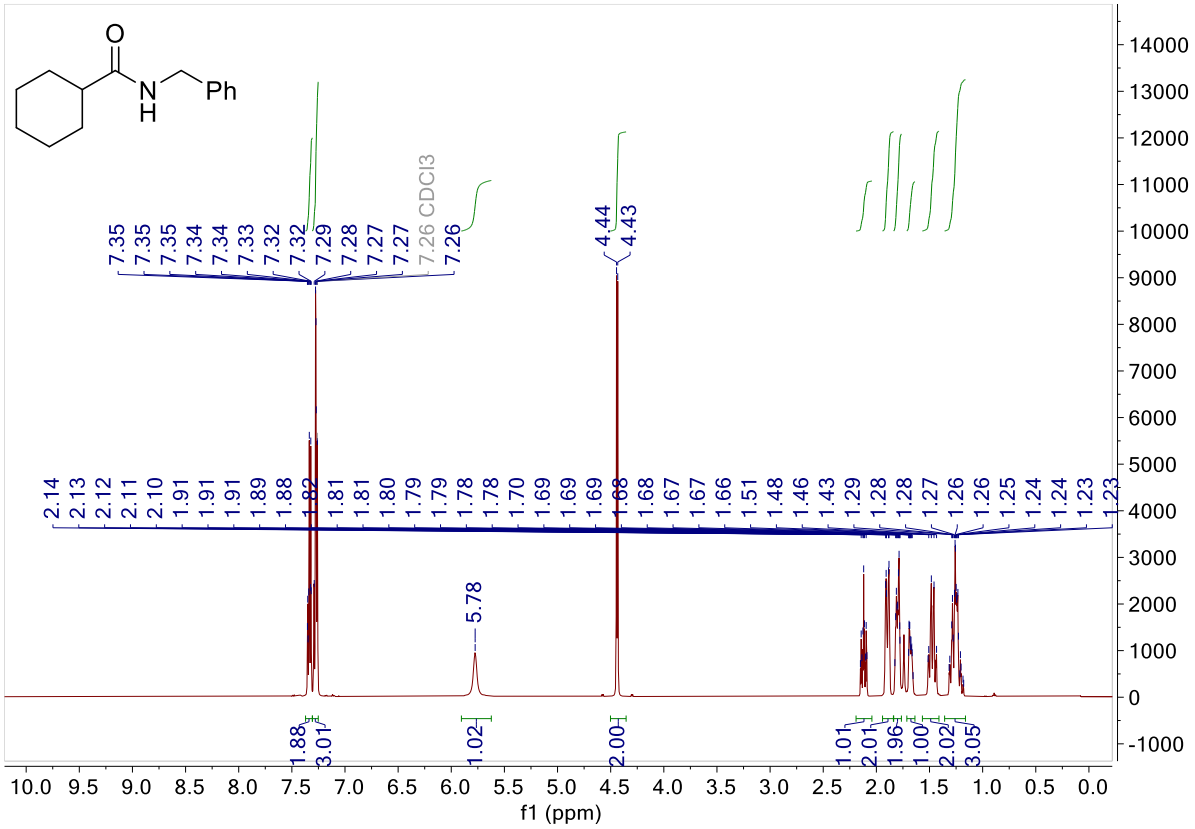


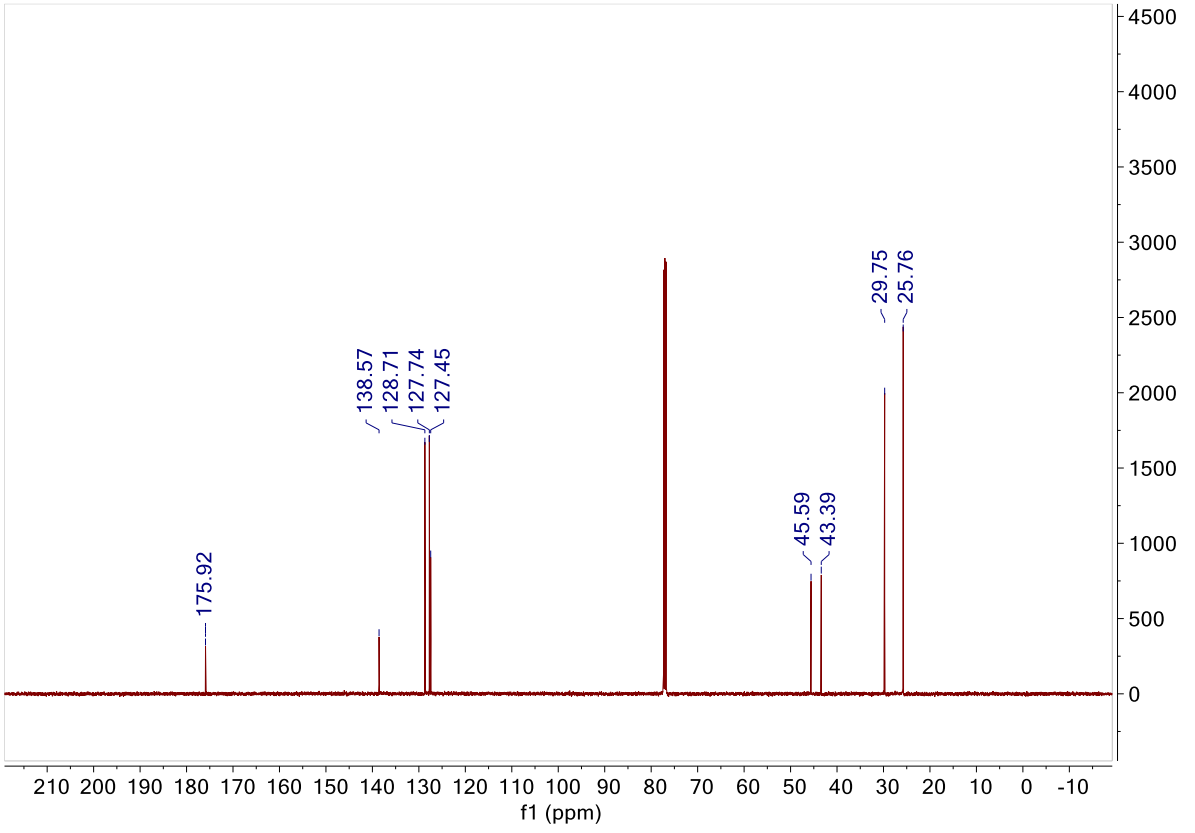



167.20
164.29
41.09
40.72
27.74
25.13
24.57
f1 (ppm)

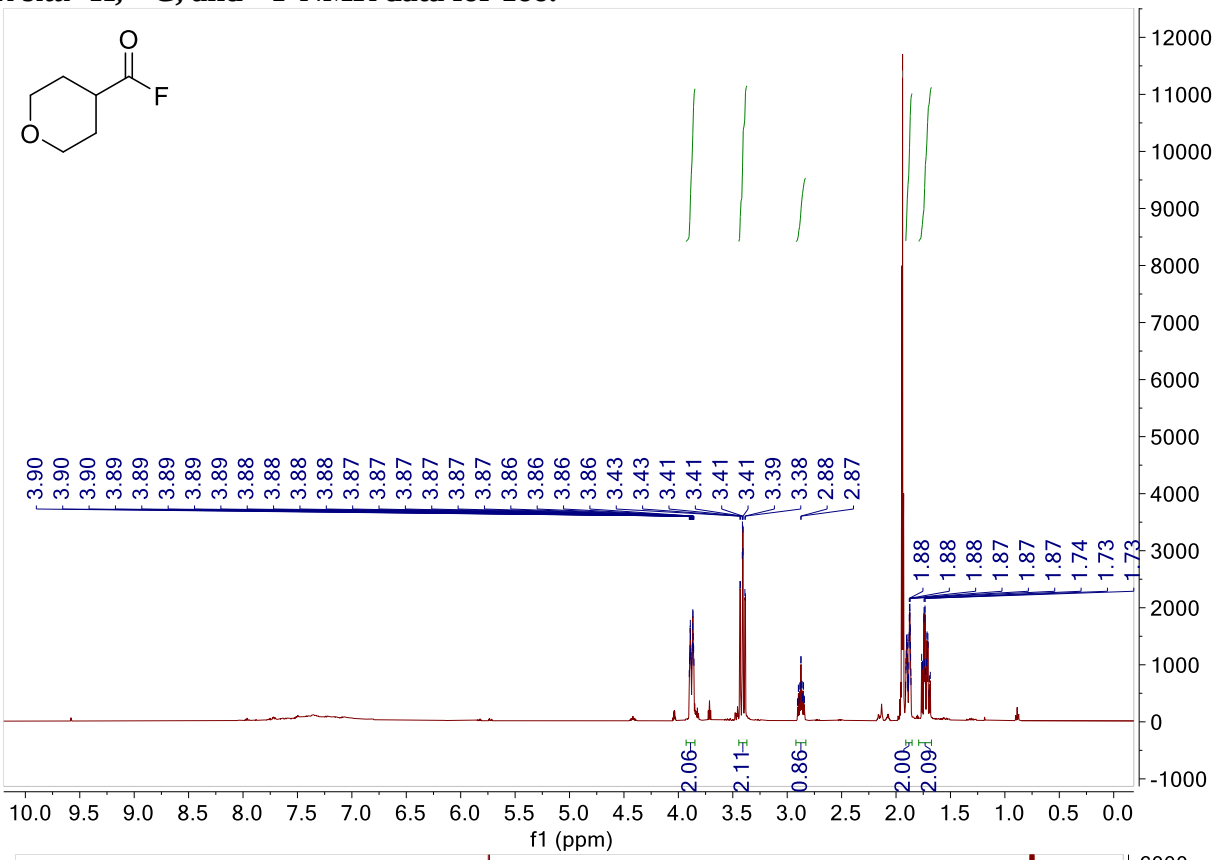

34.54
f1 (ppm)

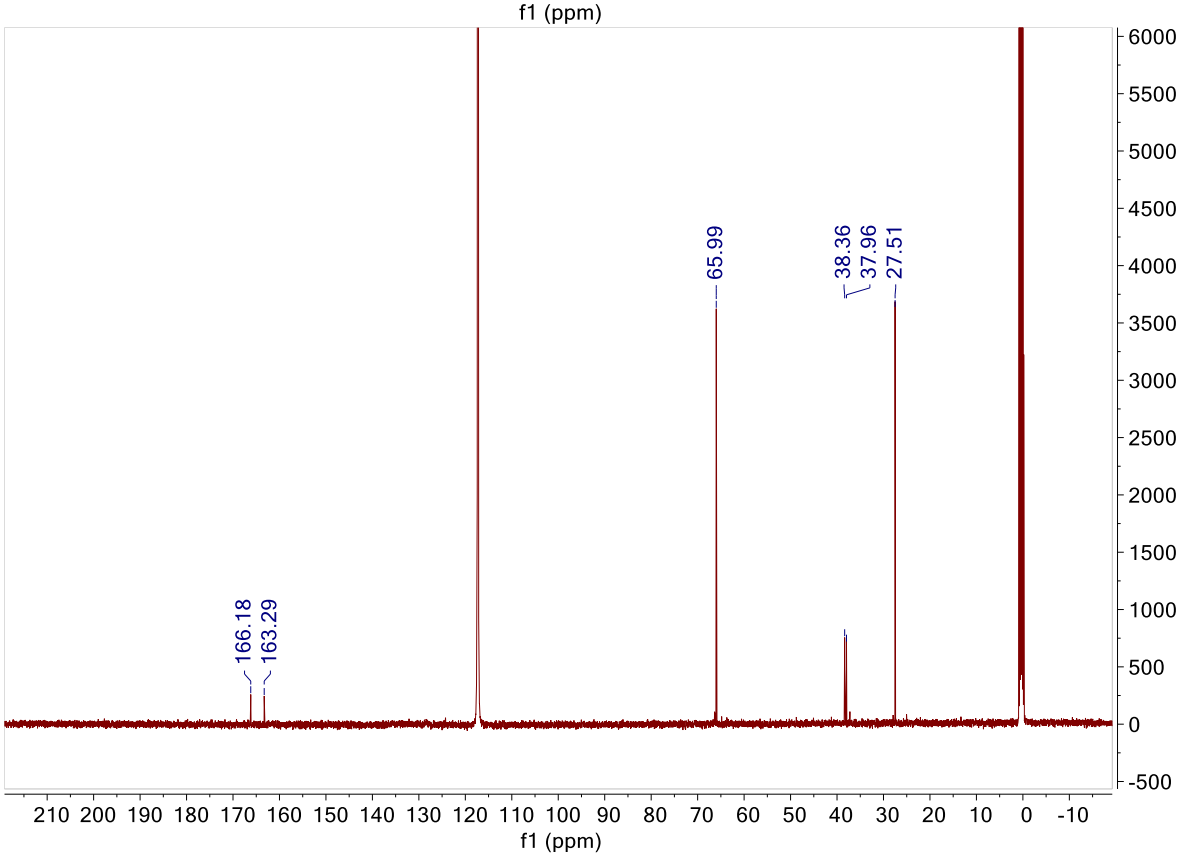
^{1}H and ^{13}C NMR data for 5nn.

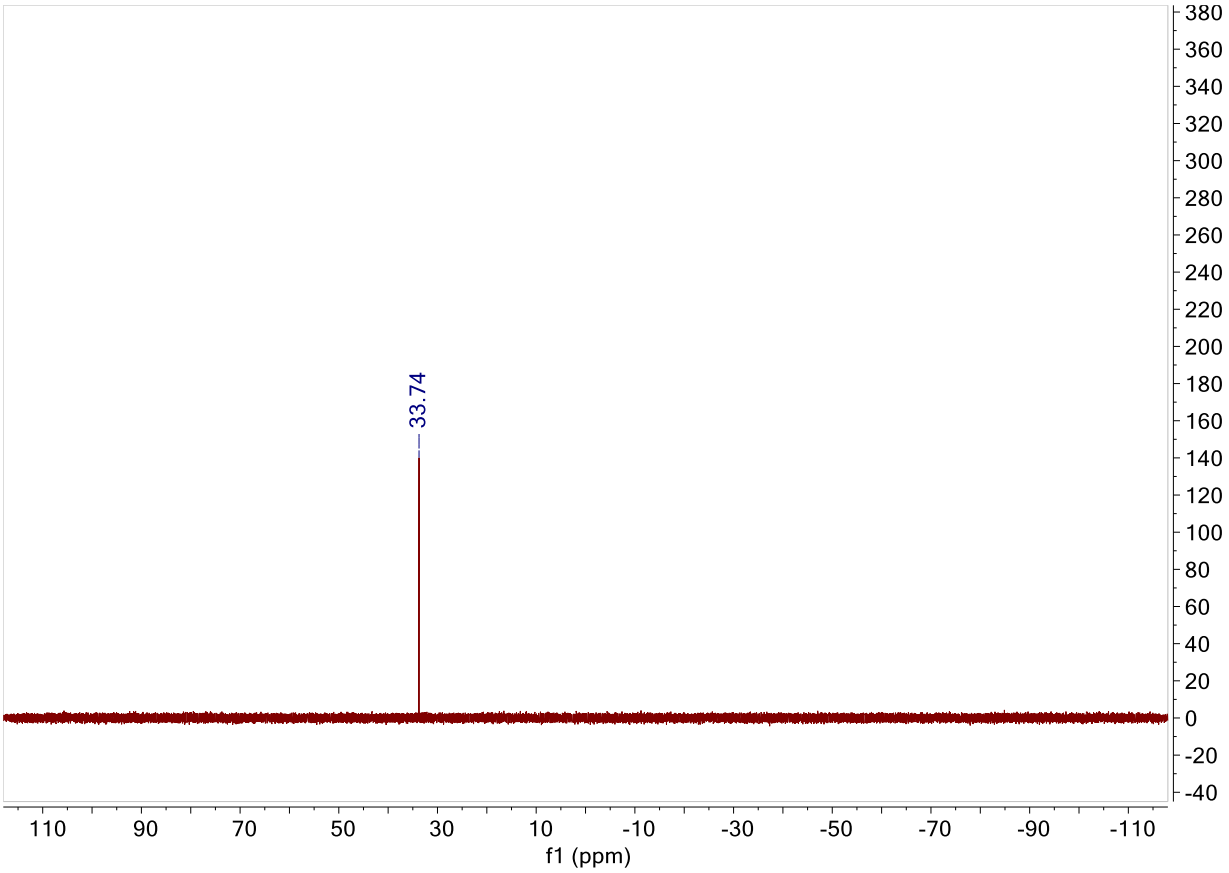




***In situ* ^{1}H, ^{13}C, and ^{19}F NMR data for 1oo.**






33.74
380
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320
300
280
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220
200
180
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120
100
80
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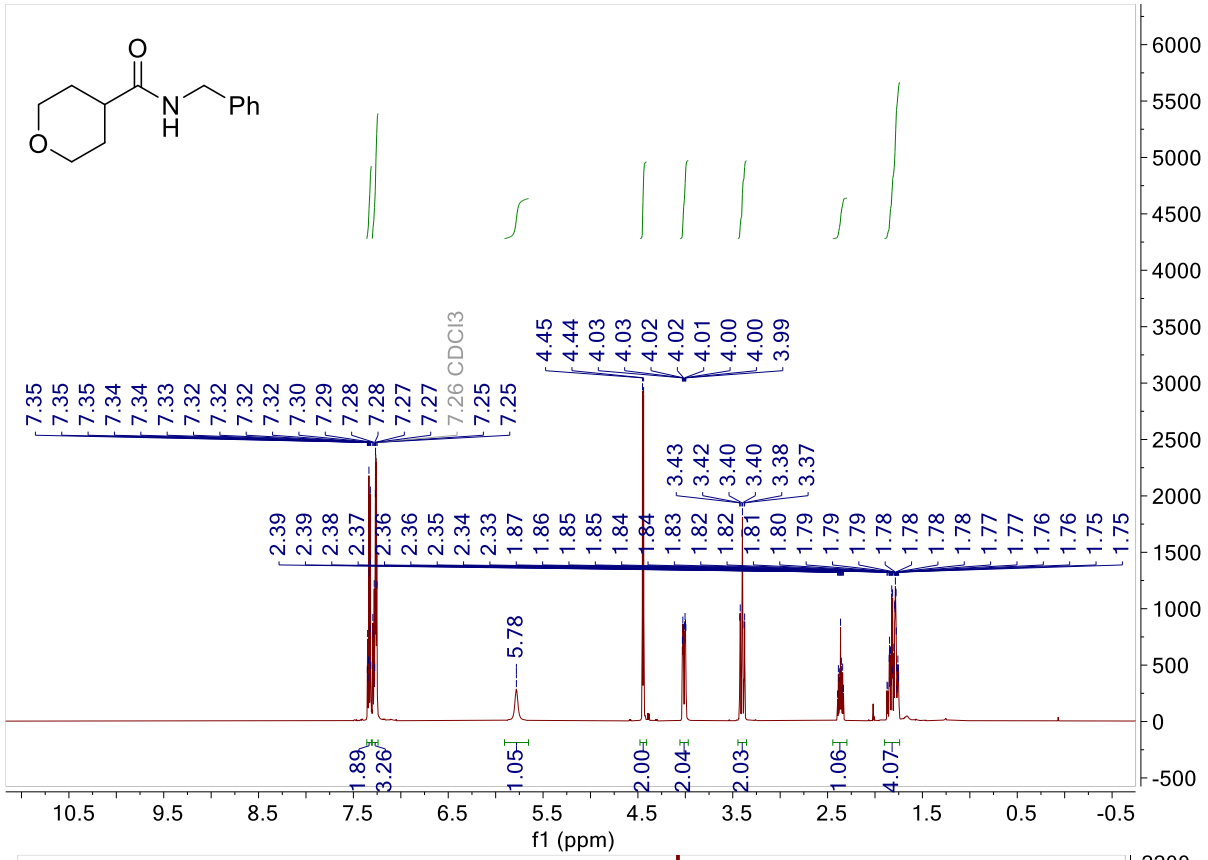
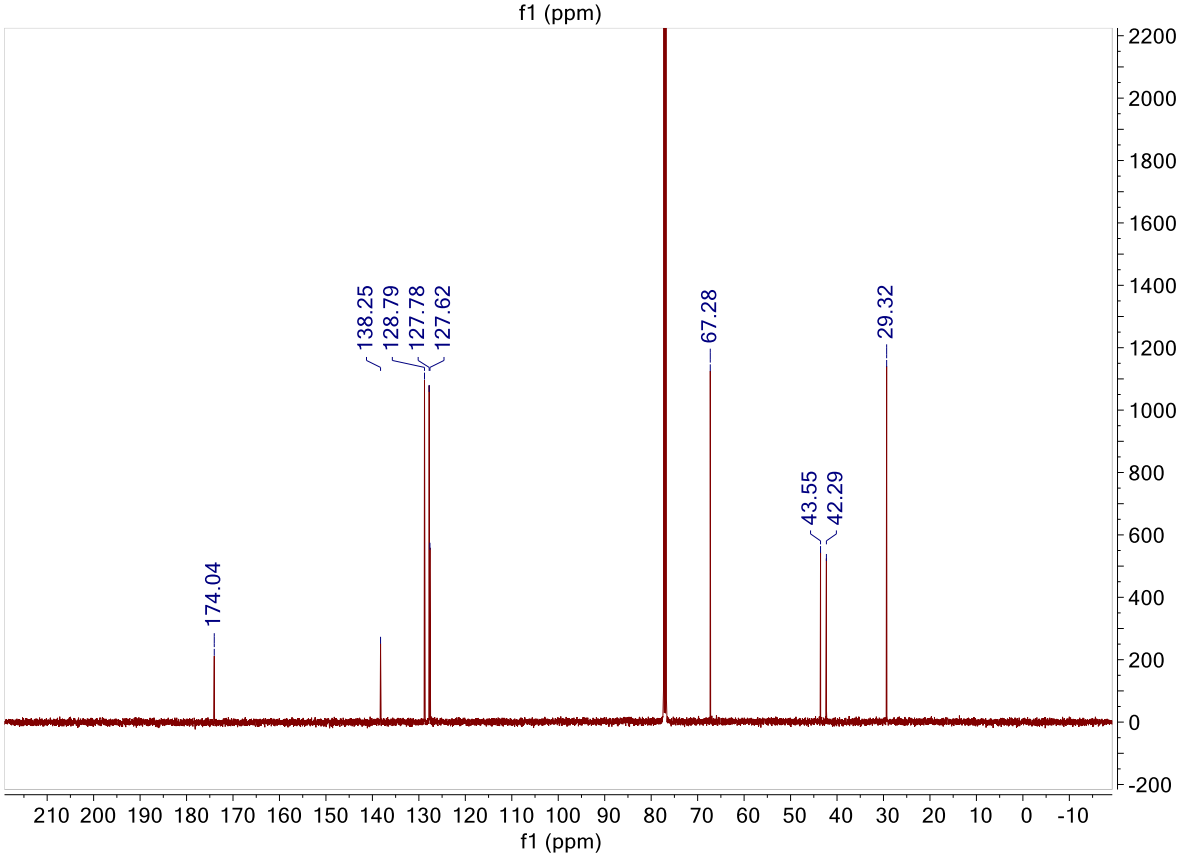
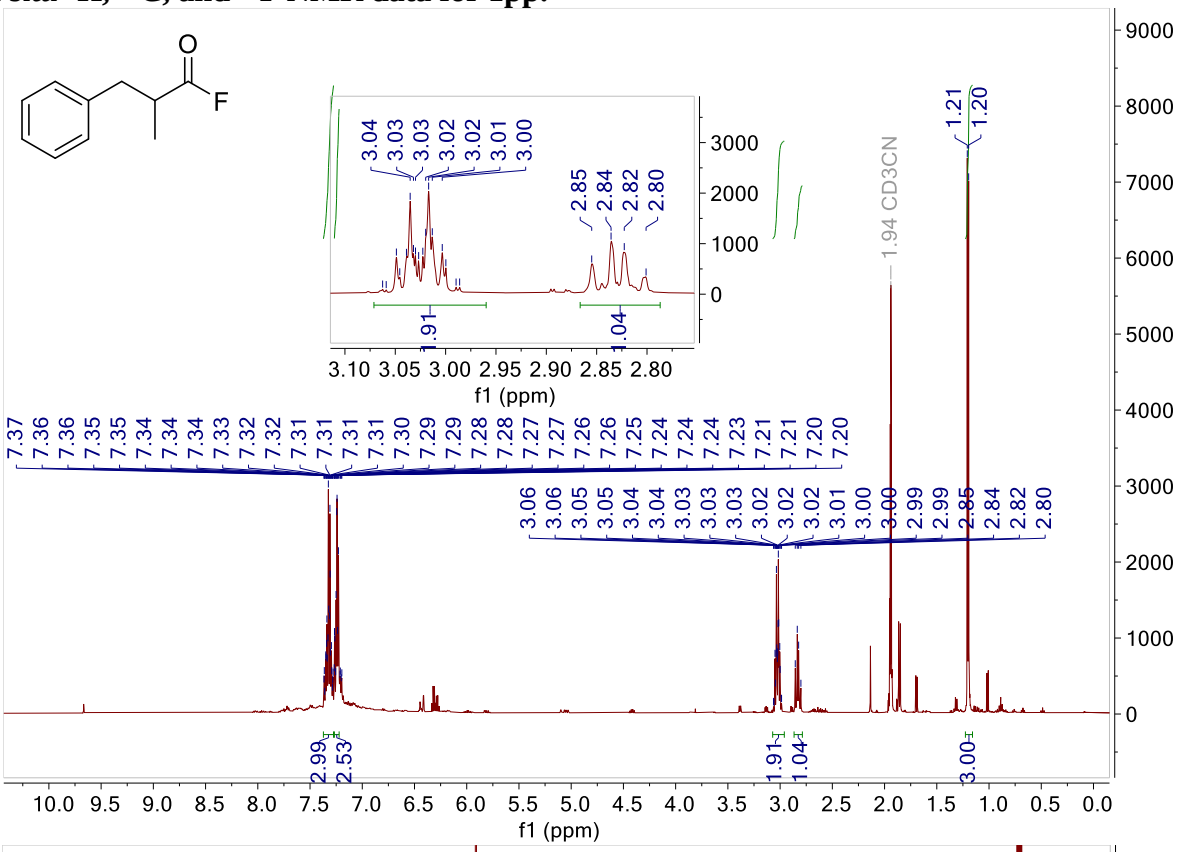
40
20
0
-20
-40
110
90
70
50
30
10
-10
-30
-50
-70
-90
-110
f1 (ppm)

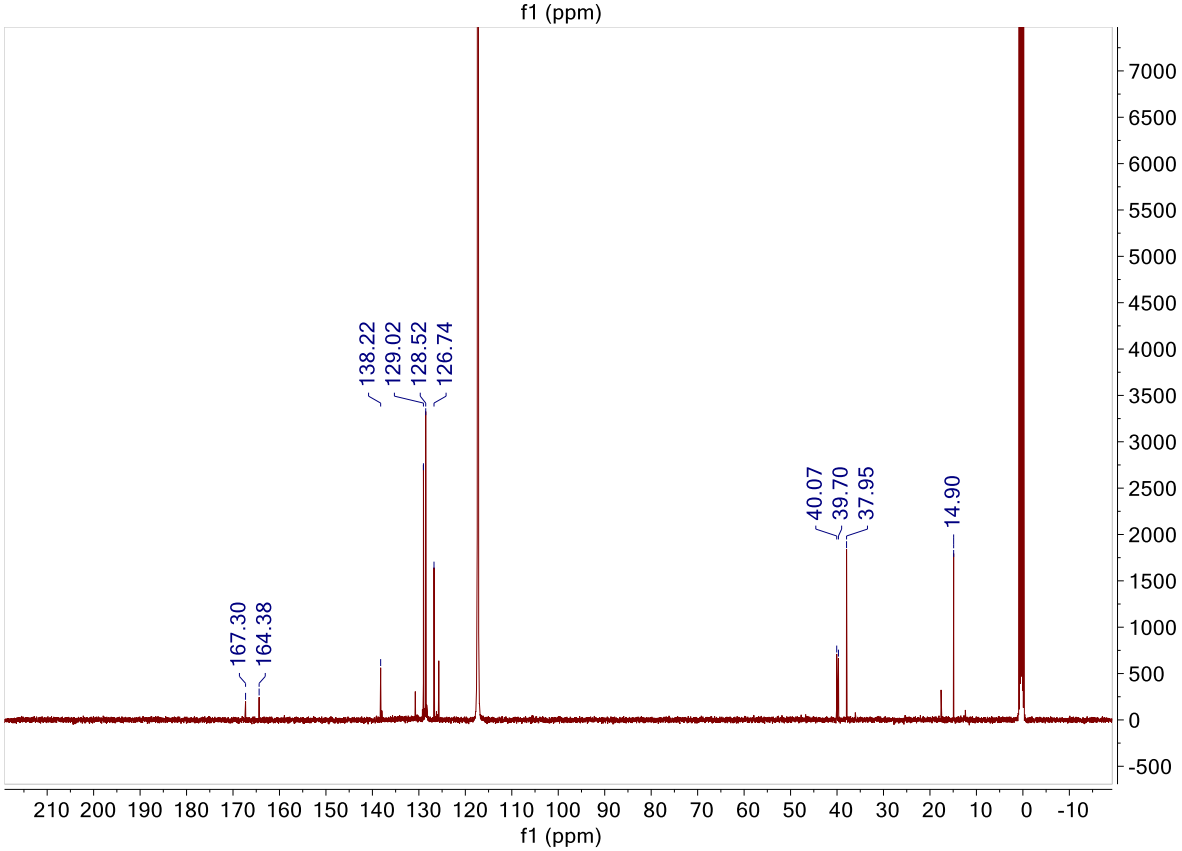
^{1}H and ^{13}C NMR data for 5oo.

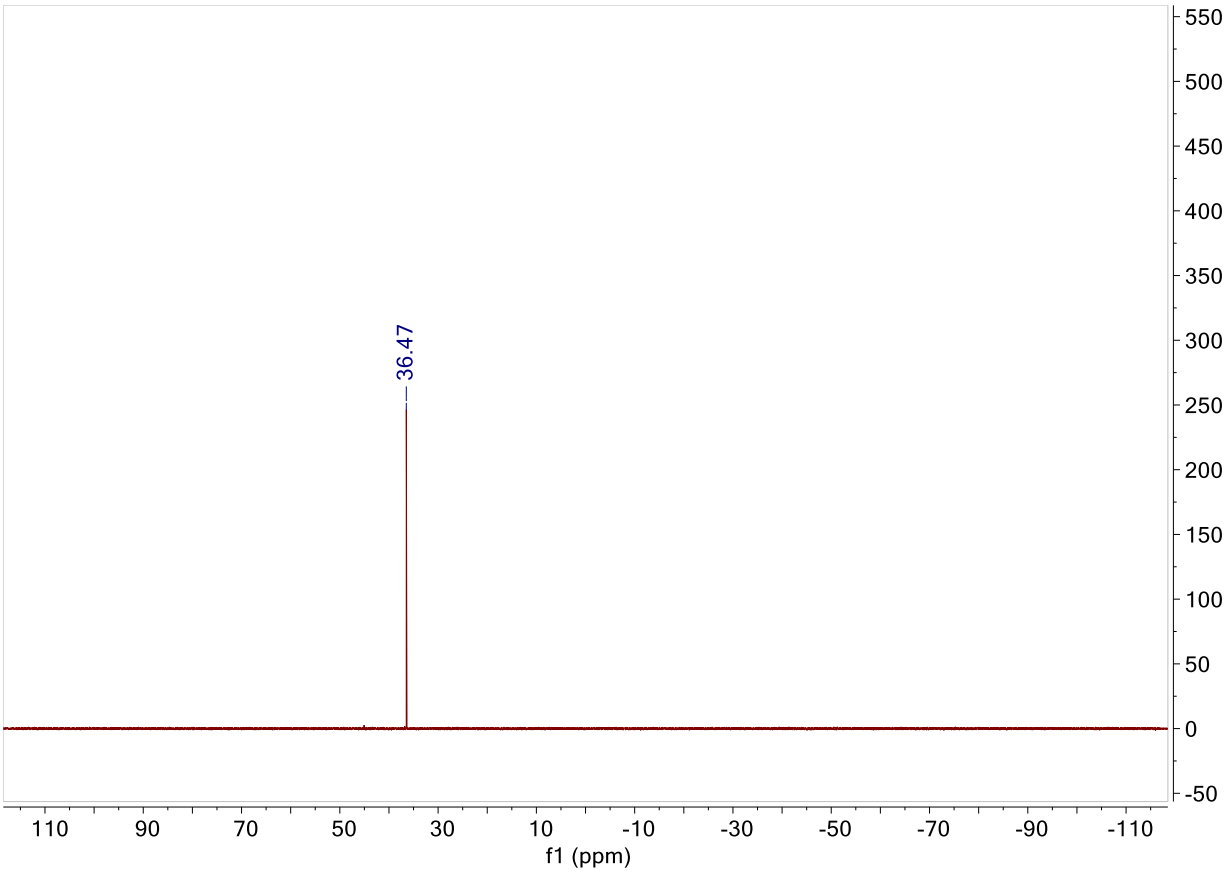




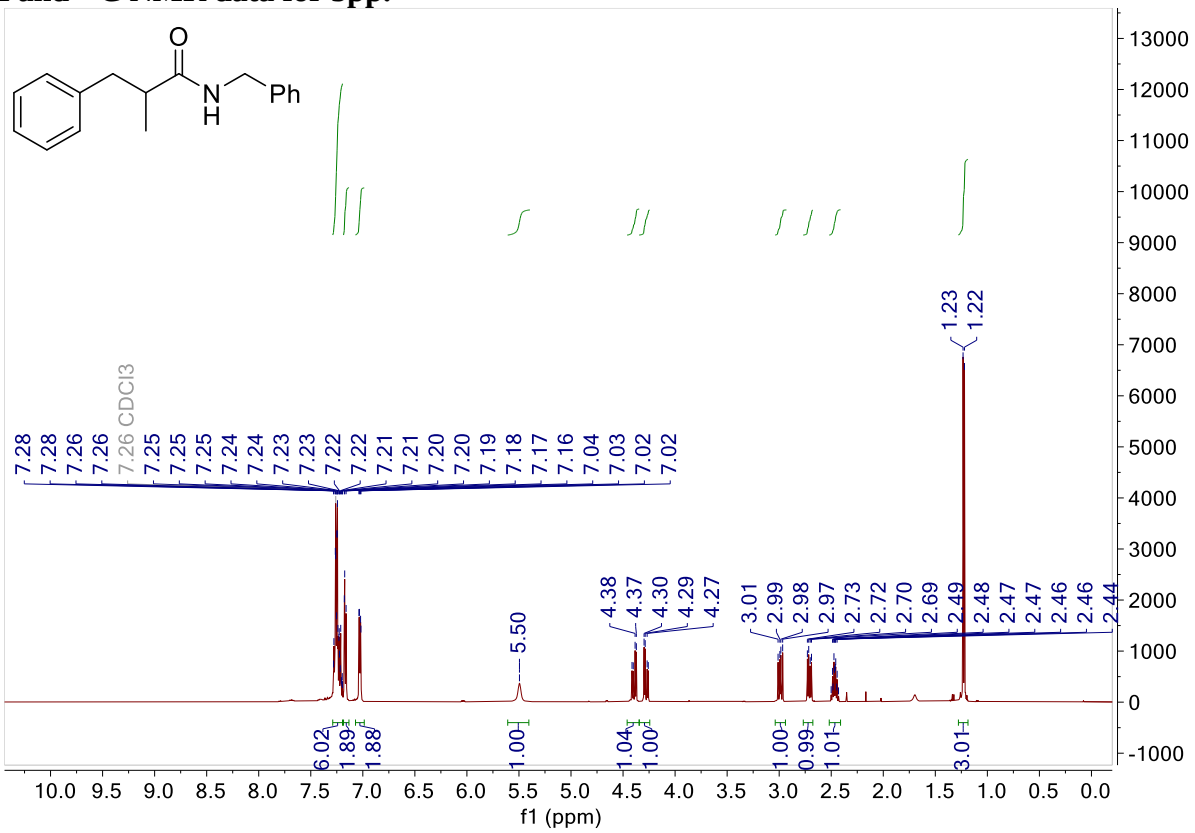
***In situ* ^{1}H, ^{13}C, and ^{19}F NMR data for 1pp.**

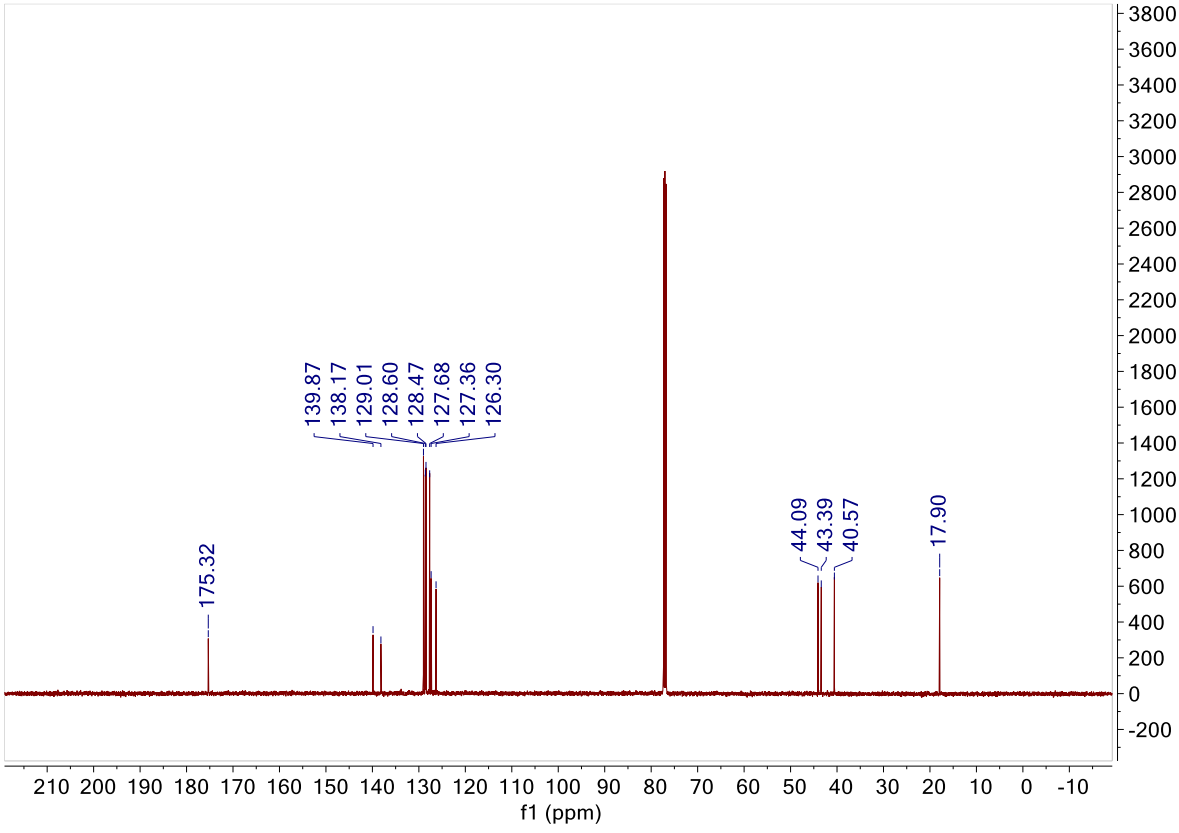




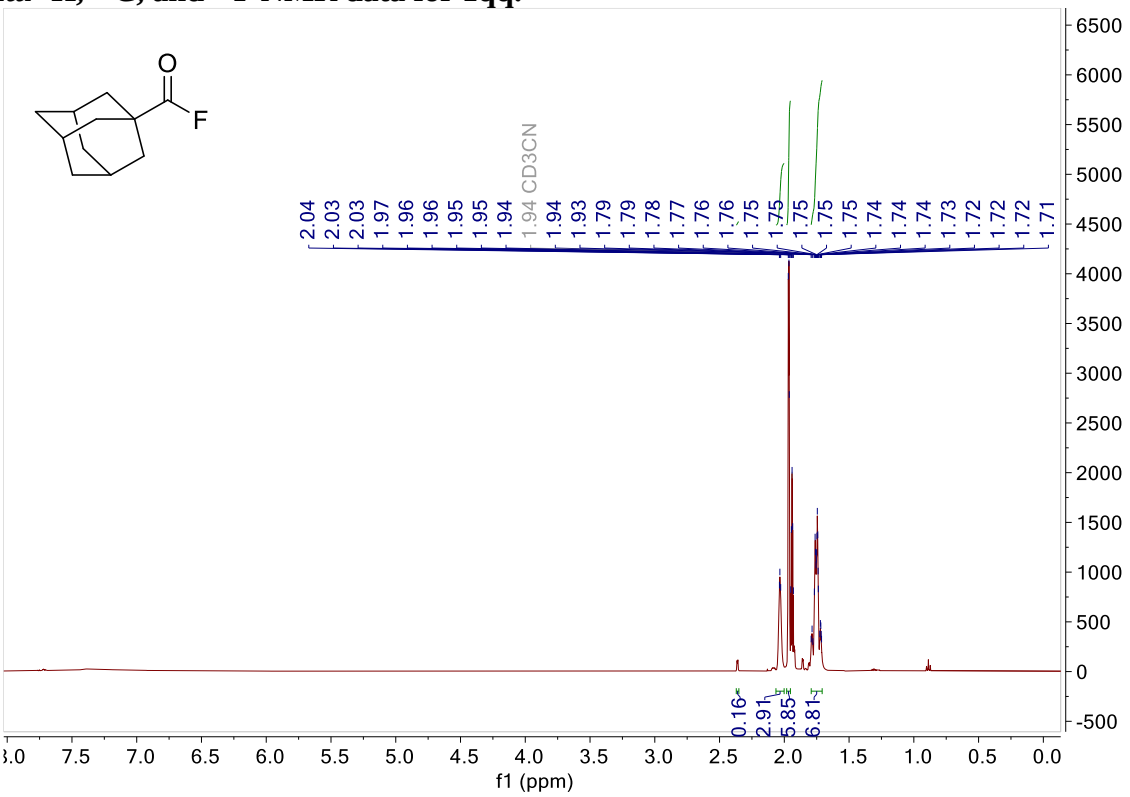

36.47
550
500
450
400
350
300
250
200
150
100
50
0
-50
110
90
70
50
30
10
-10
-30
-50
-70
-90
-110
f1 (ppm)

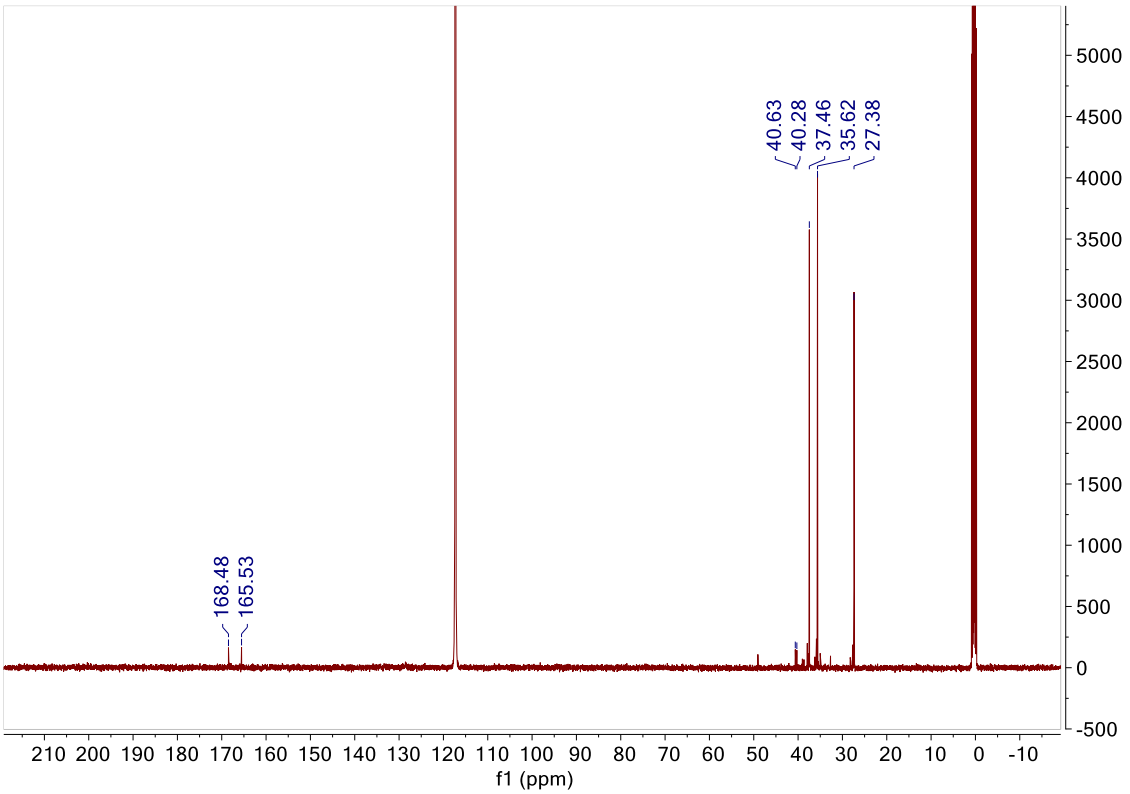
^{1}H and ^{13}C NMR data for 5pp.

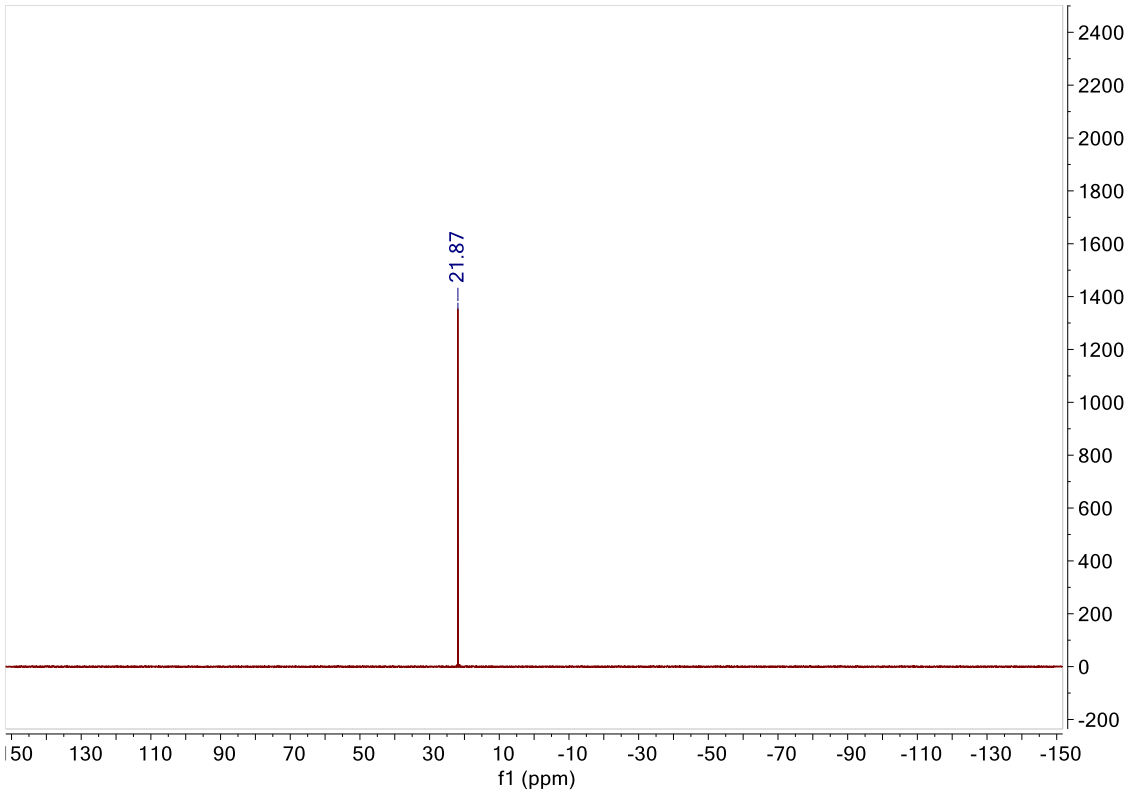




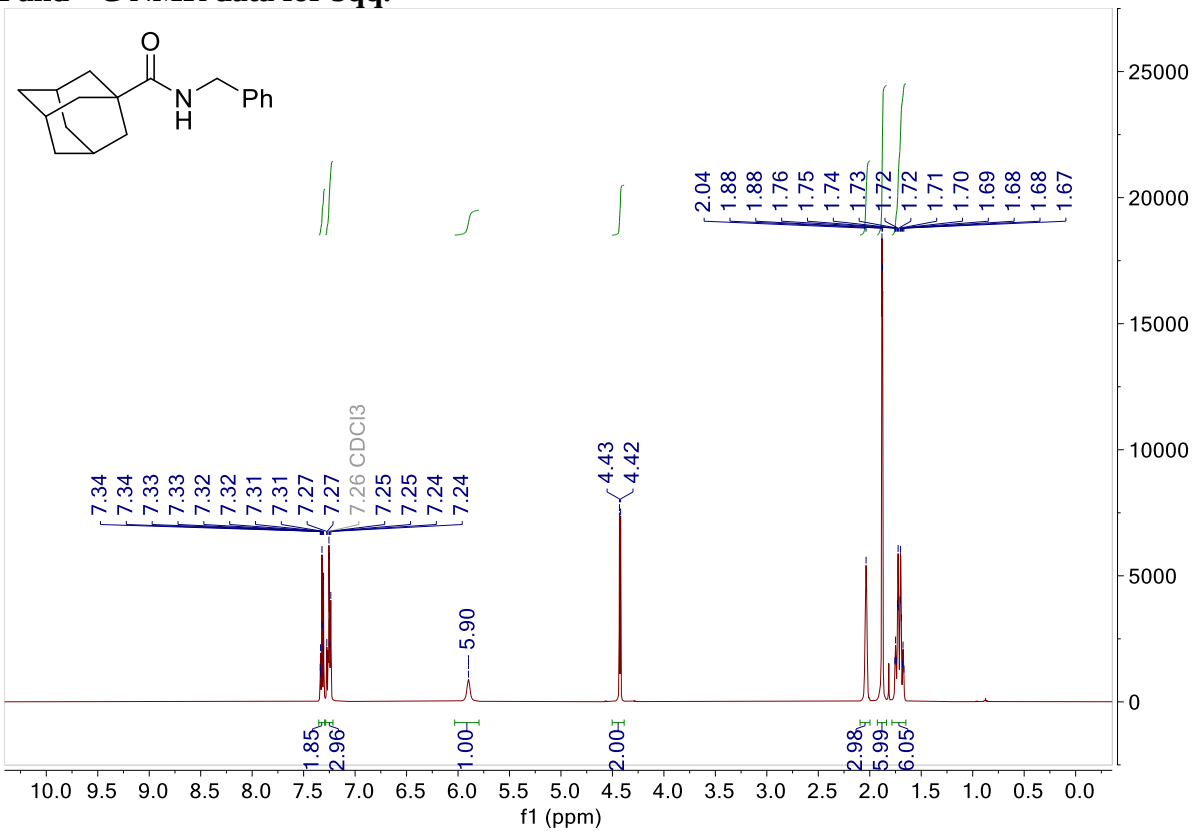
***In situ* ^{1}H, ^{13}C, and ^{19}F NMR data for 1qq.**

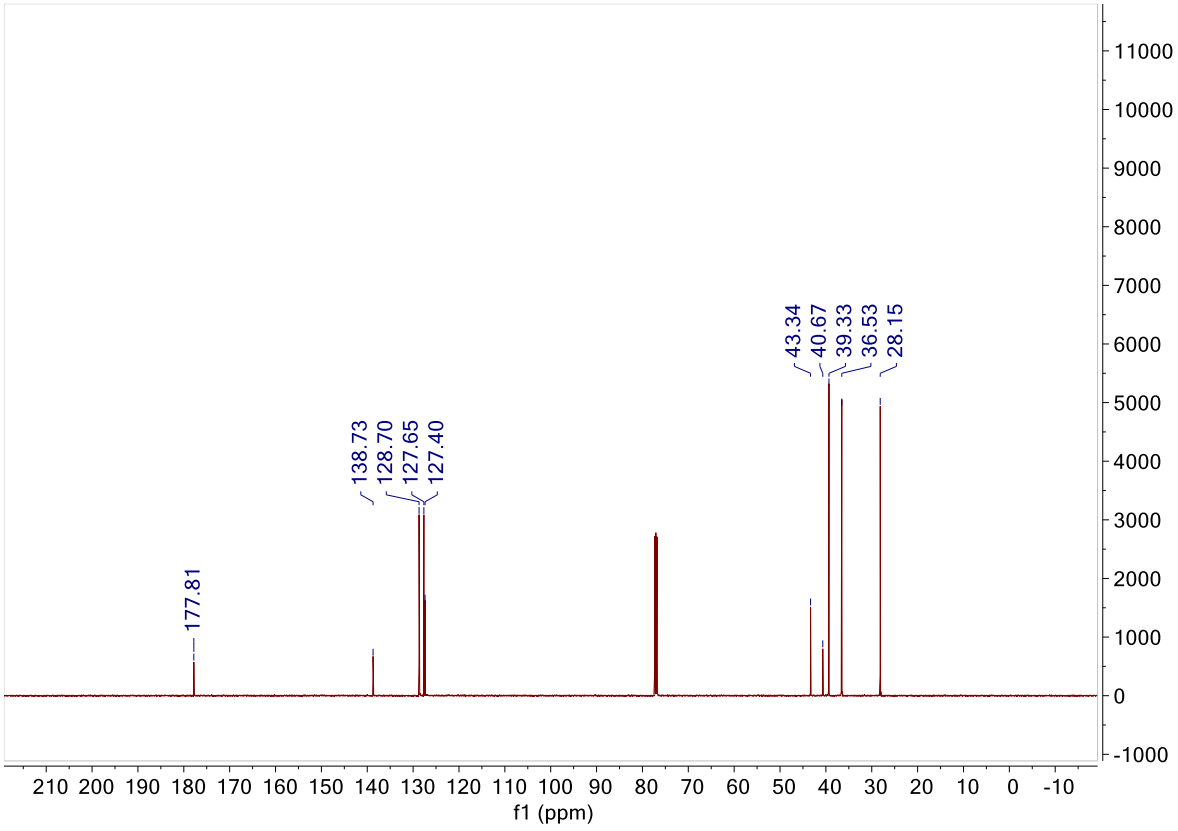




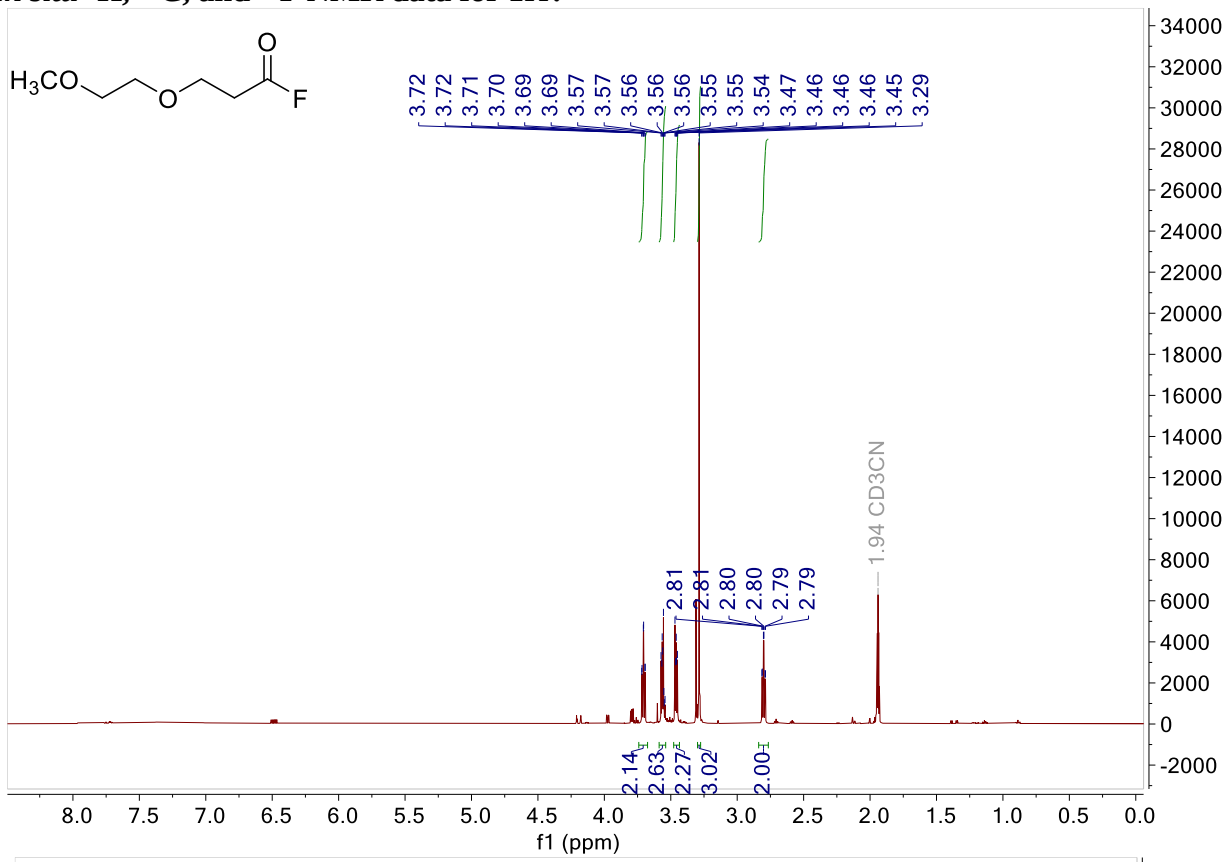

21.87
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
50
130
110
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
f1 (ppm)

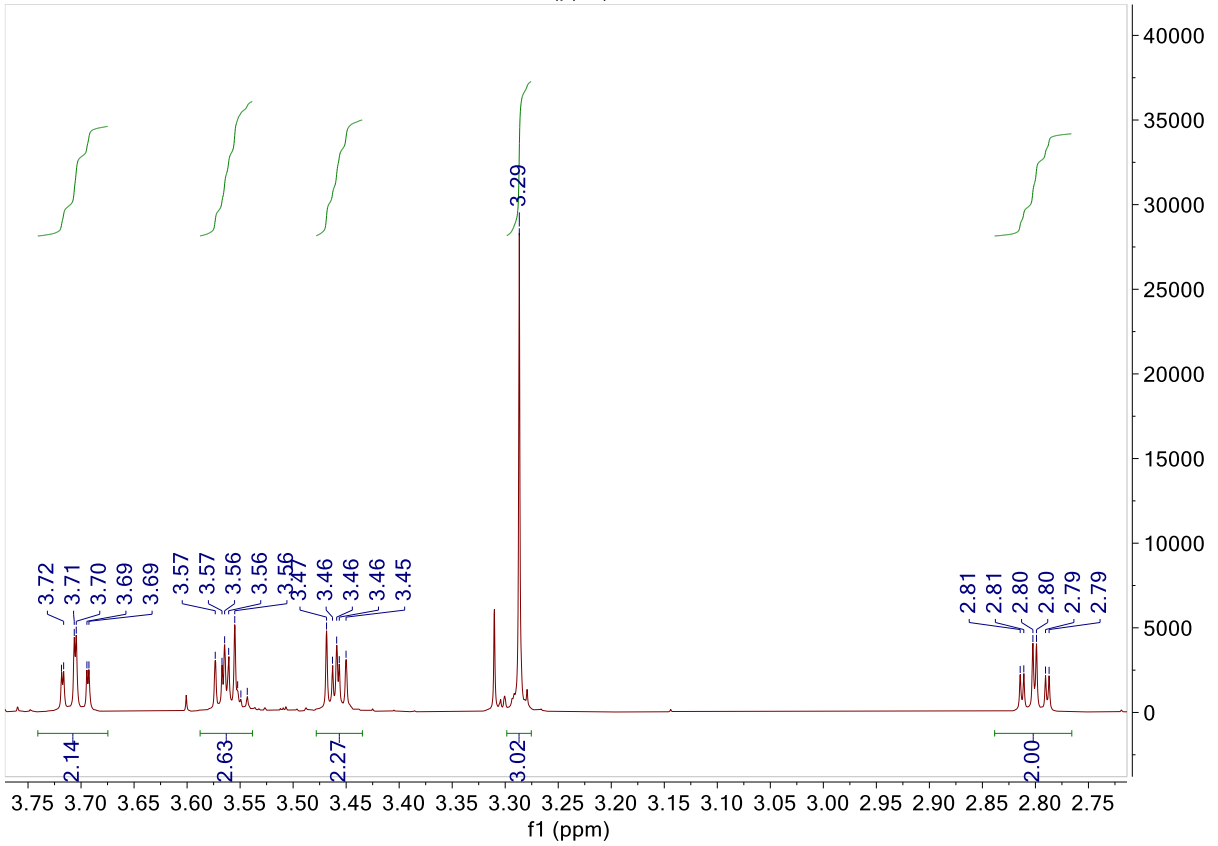
^{1}H and ^{13}C NMR data for 5qq.

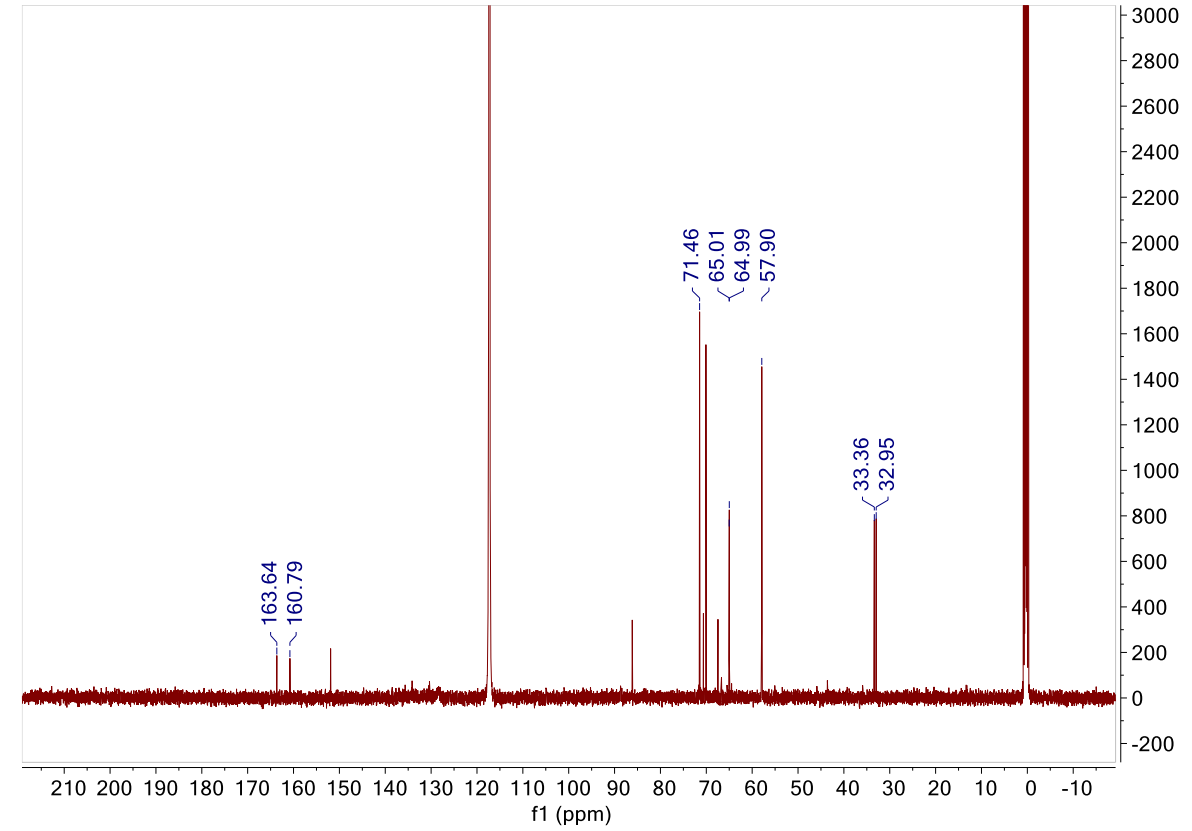


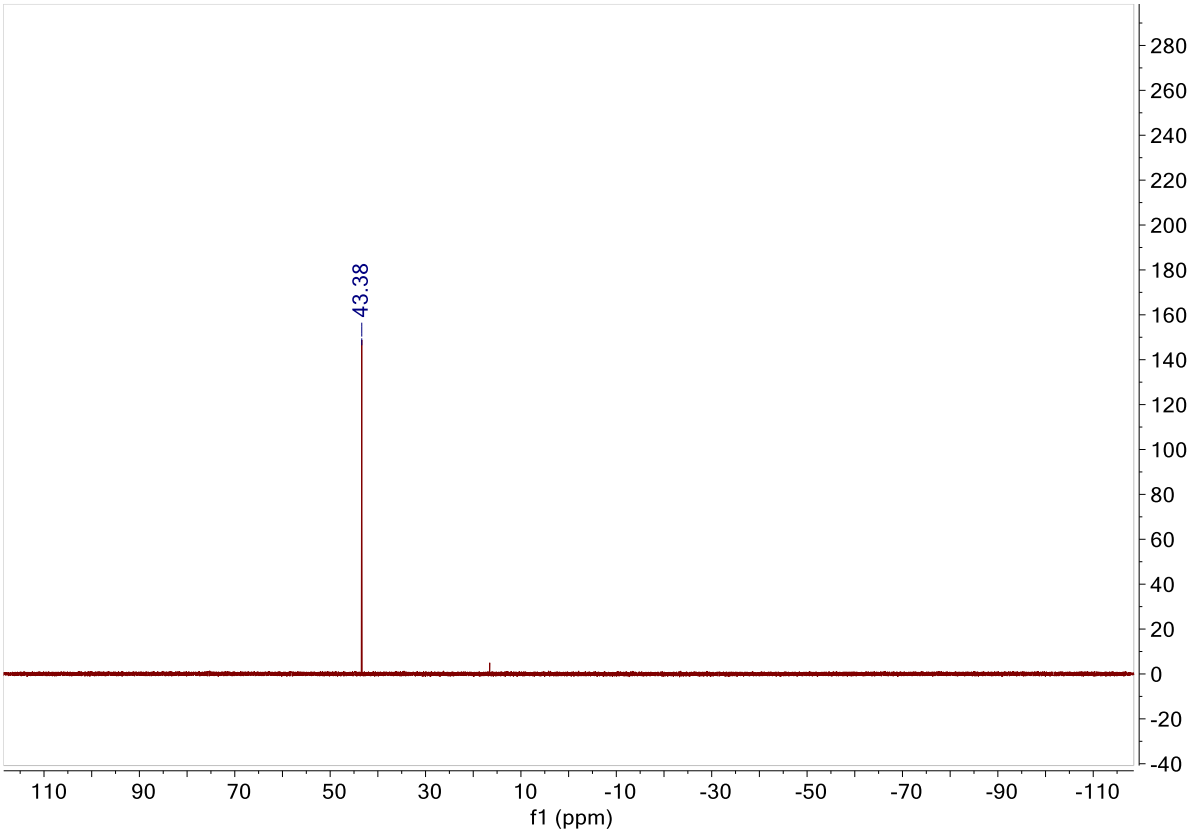


***In situ* ^{1}H, ^{13}C, and ^{19}F NMR data for 1rr.**

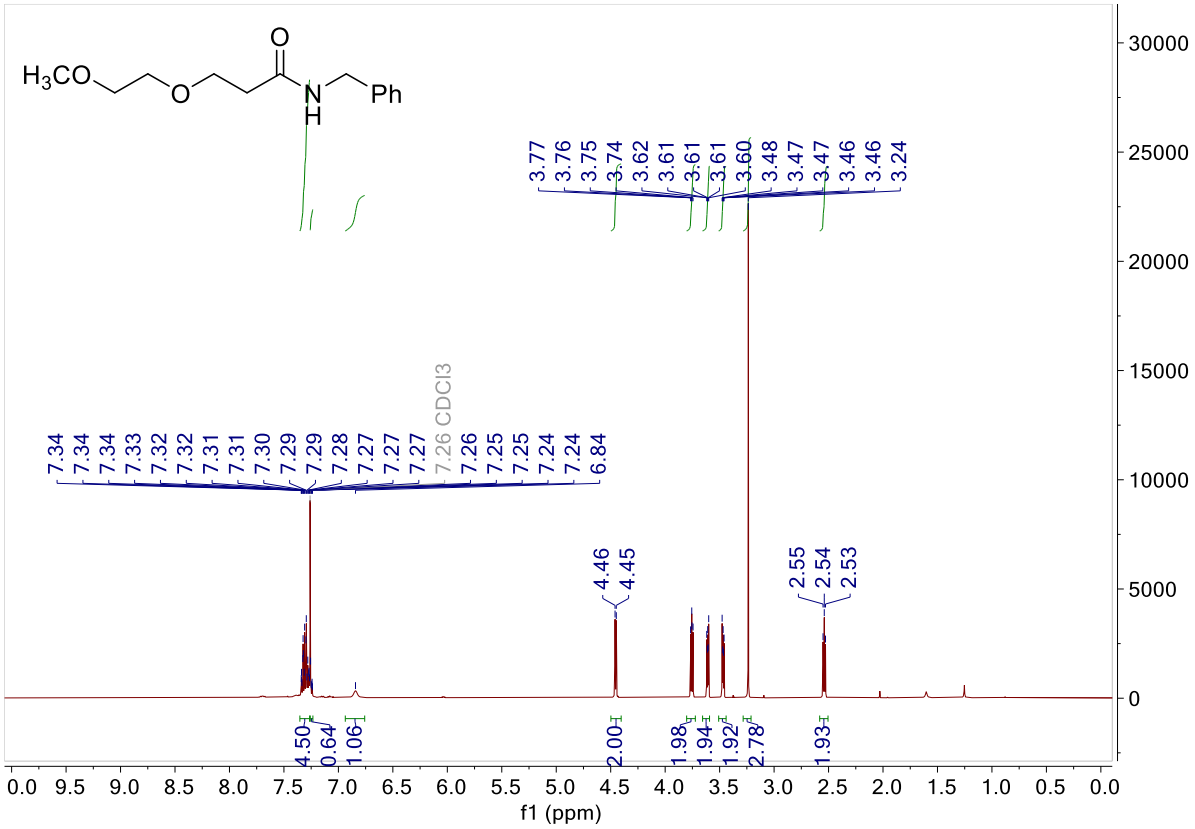


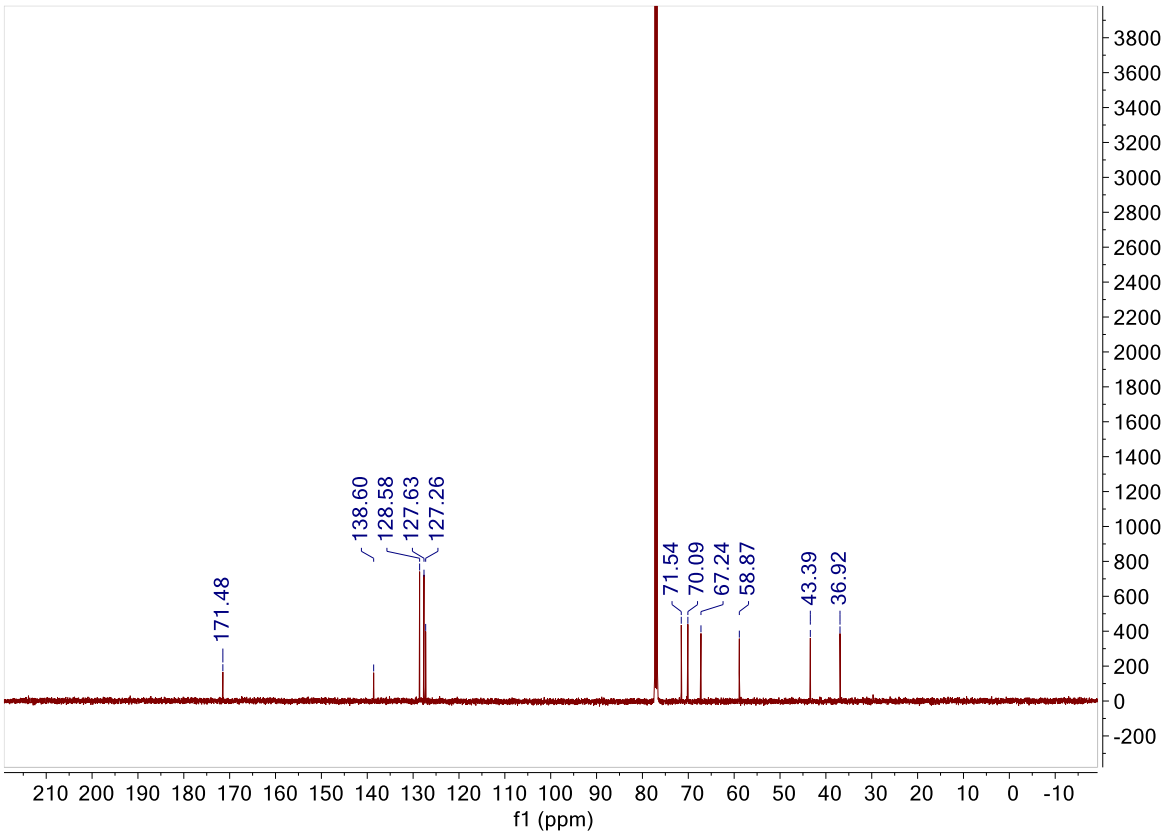



163.64
160.79
71.46
65.01
64.99
57.90
33.36
32.95
f1 (ppm)

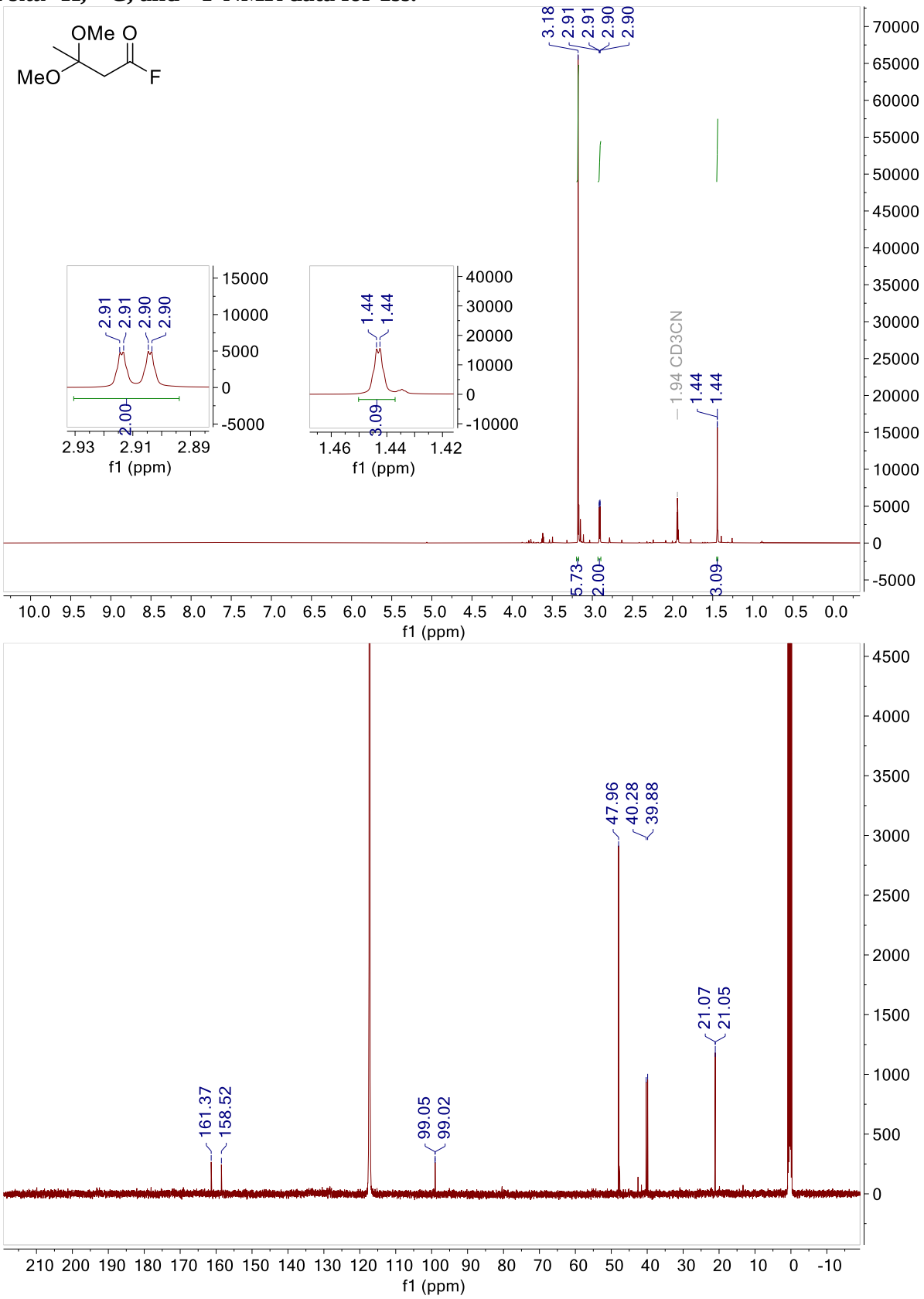

43.38
f1 (ppm)

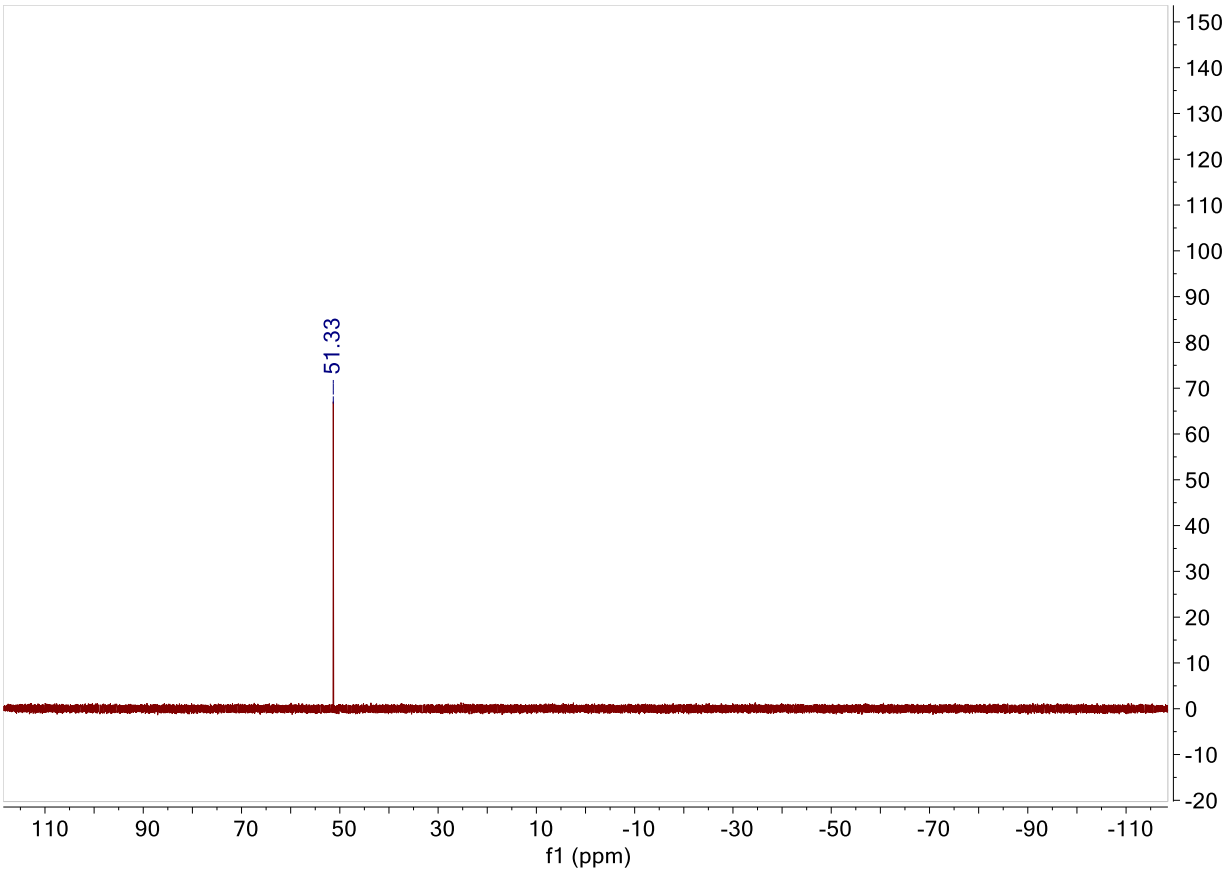
^{1}H and ^{13}C NMR data for 5rr.



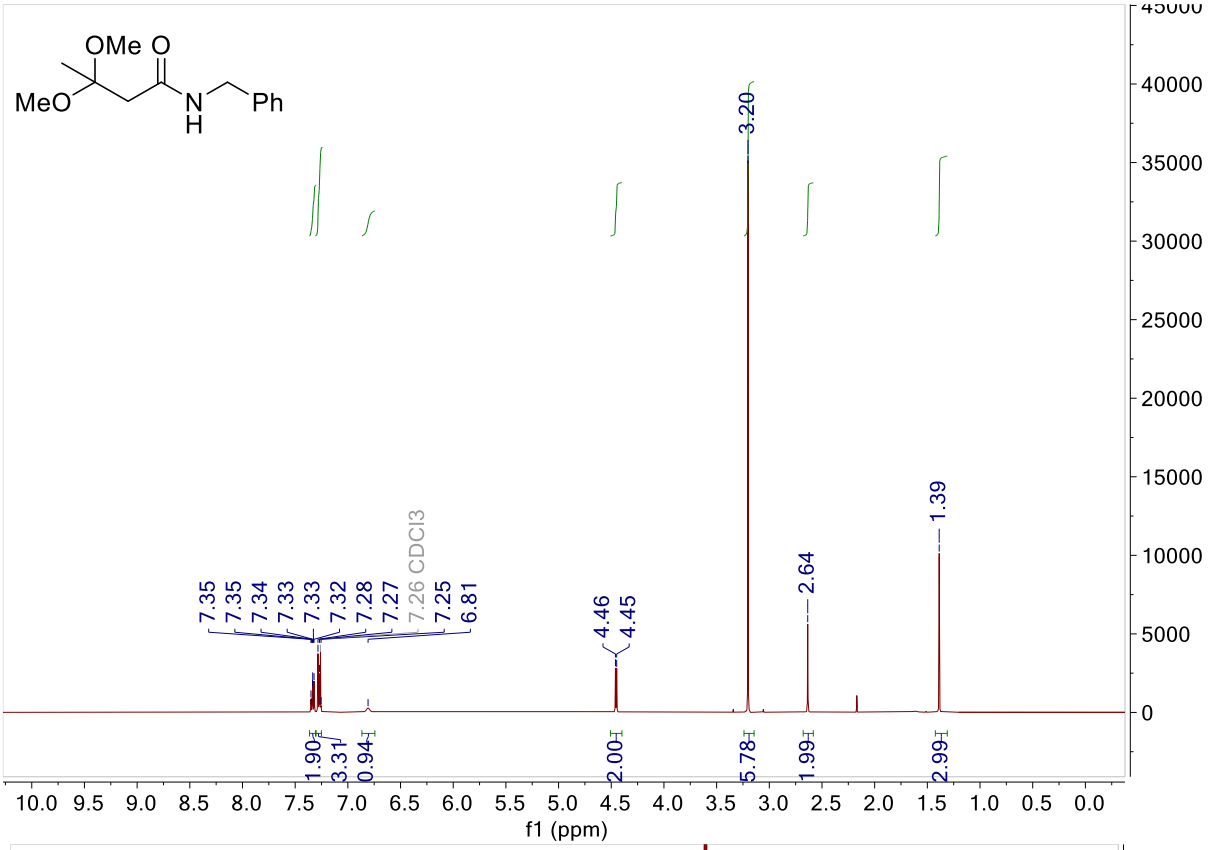


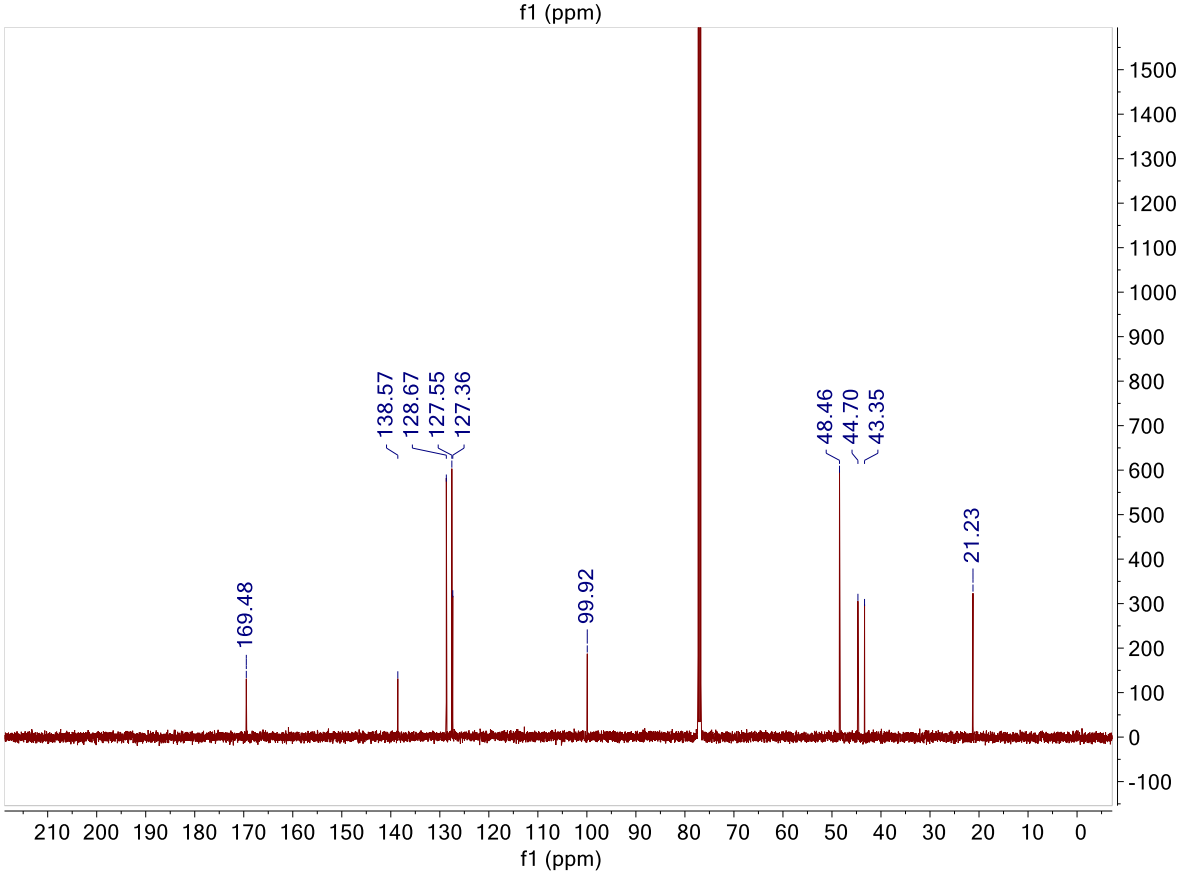
***In situ* ^{1}H, ^{13}C, and ^{19}F NMR data for 1ss.**



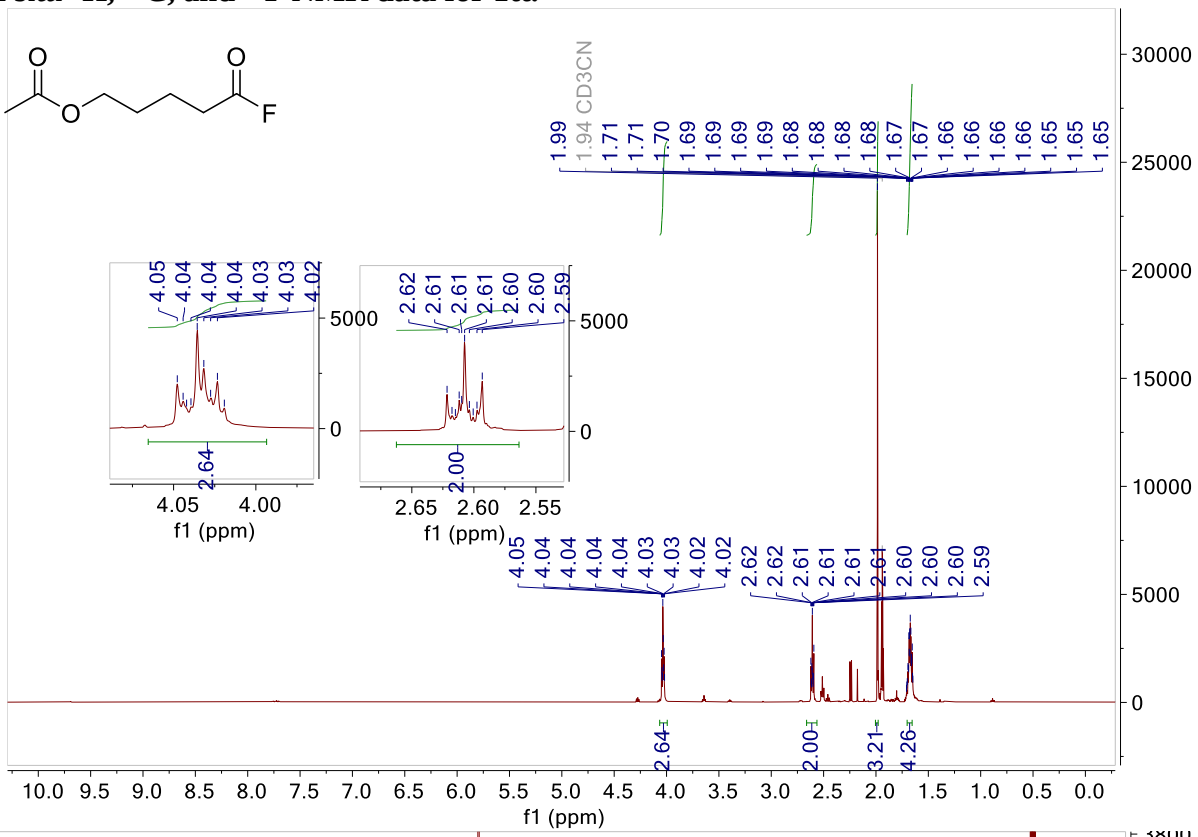

51.33
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
110
90
70
50
30
10
-10
-30
-50
-70
-90
-110
f1 (ppm)

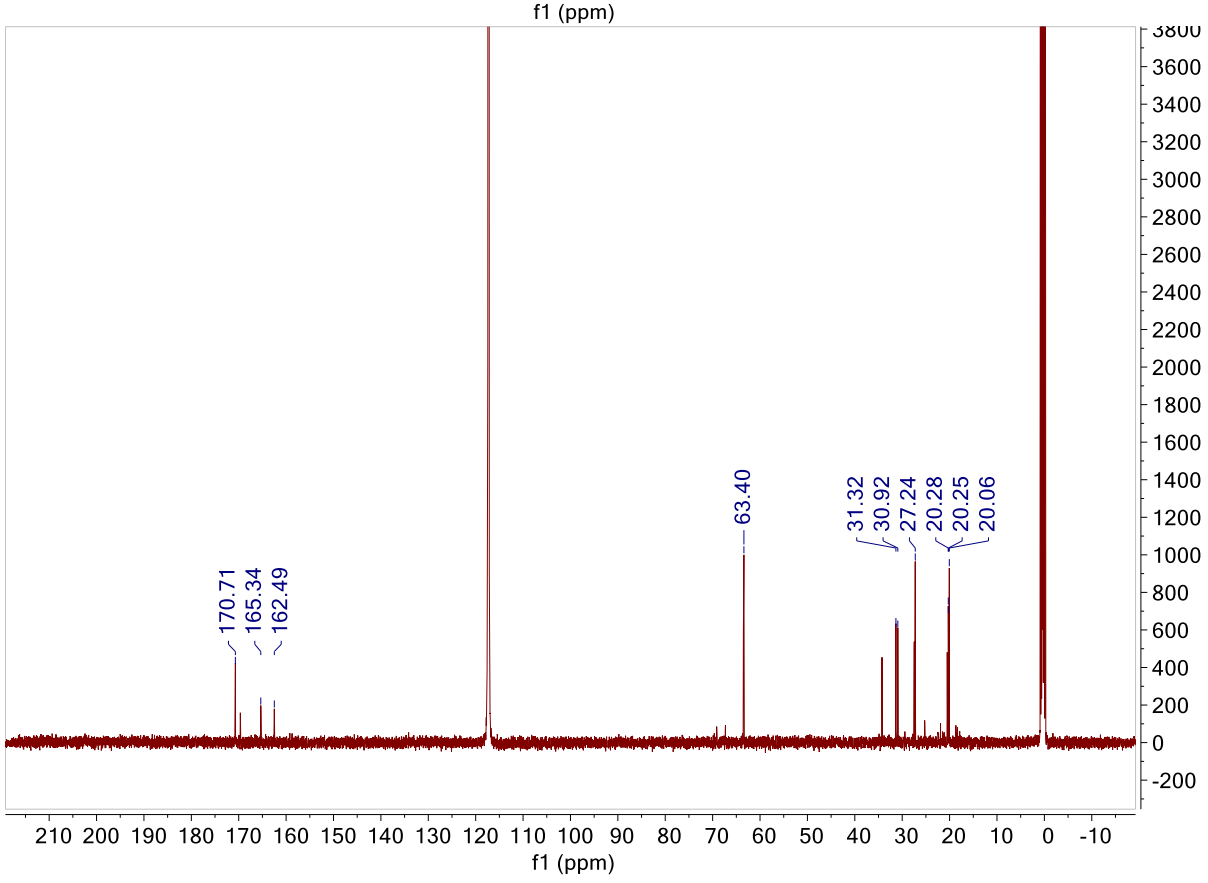
^{1}H and ^{13}C NMR data for 5ss.

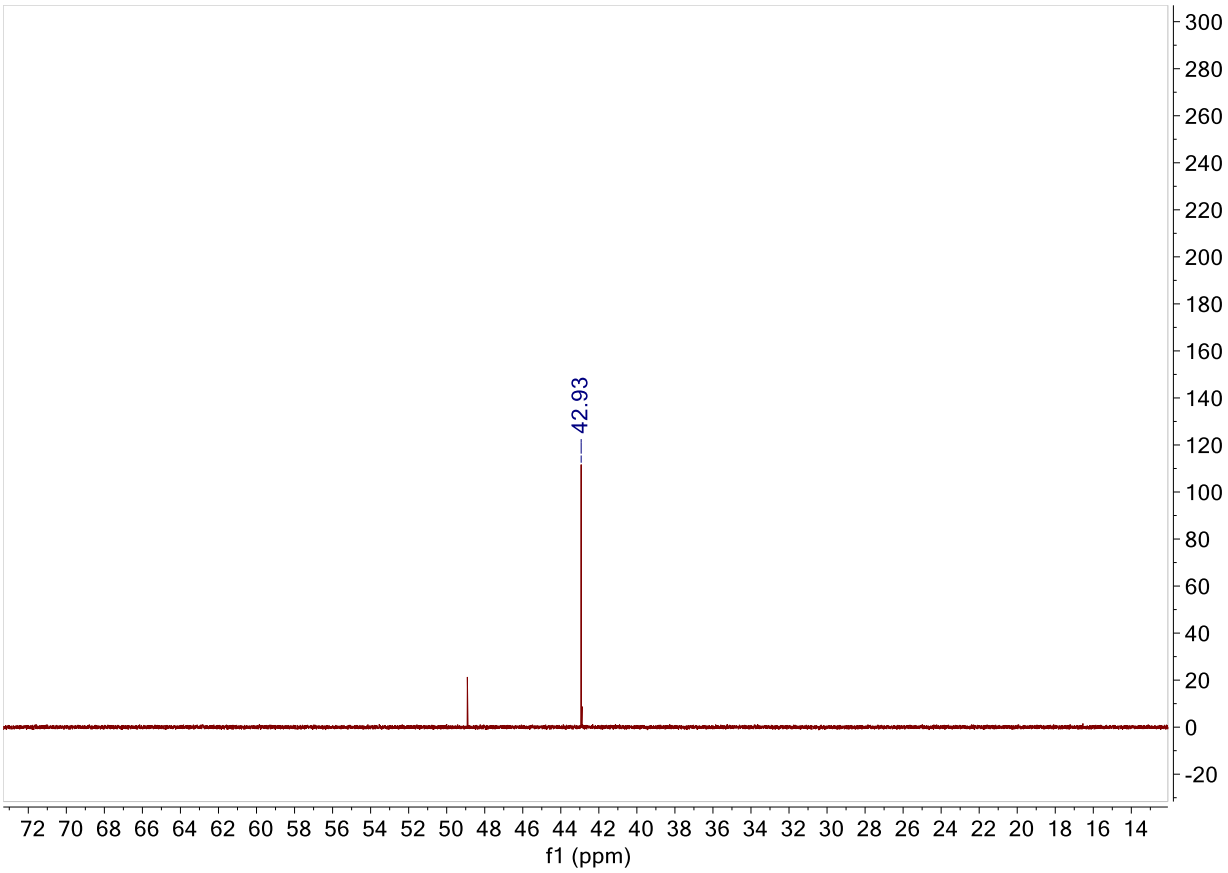




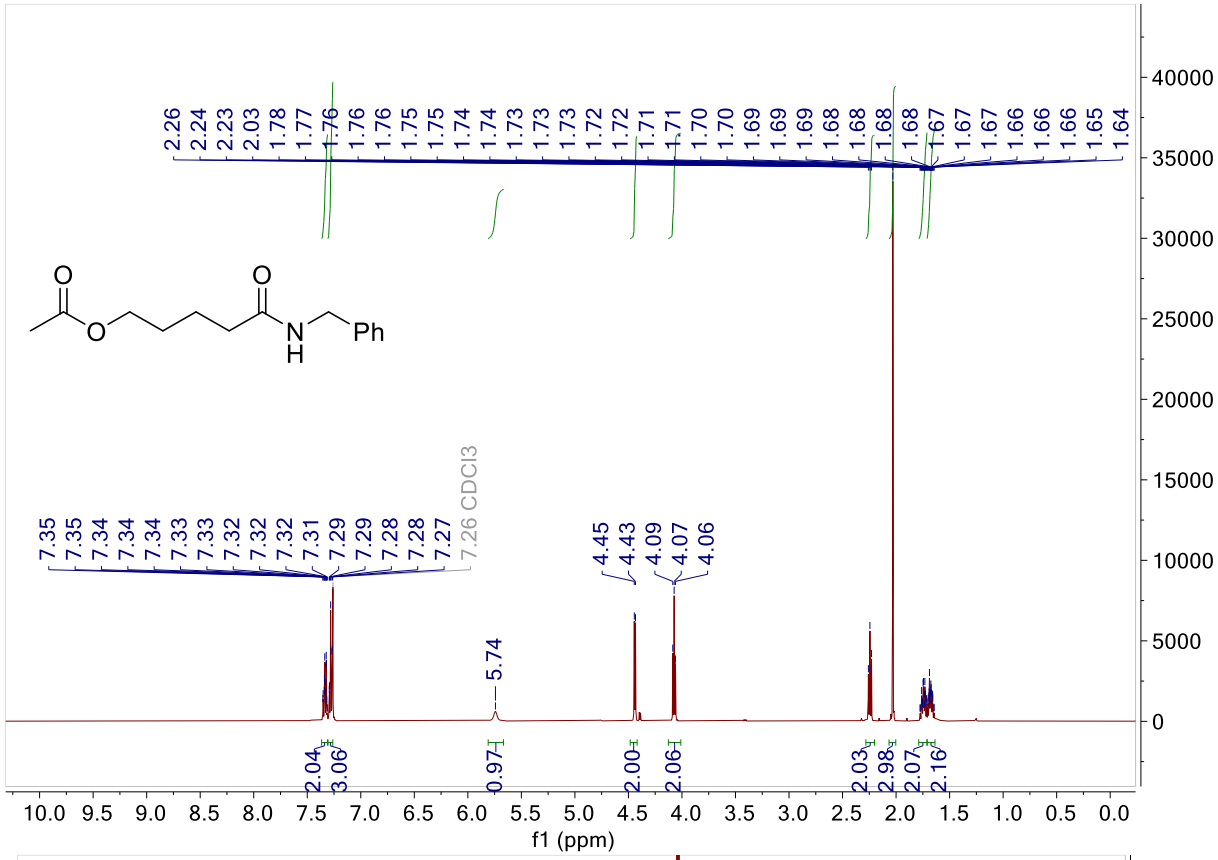
***In situ* ^{1}H, ^{13}C, and ^{19}F NMR data for 1tt.**

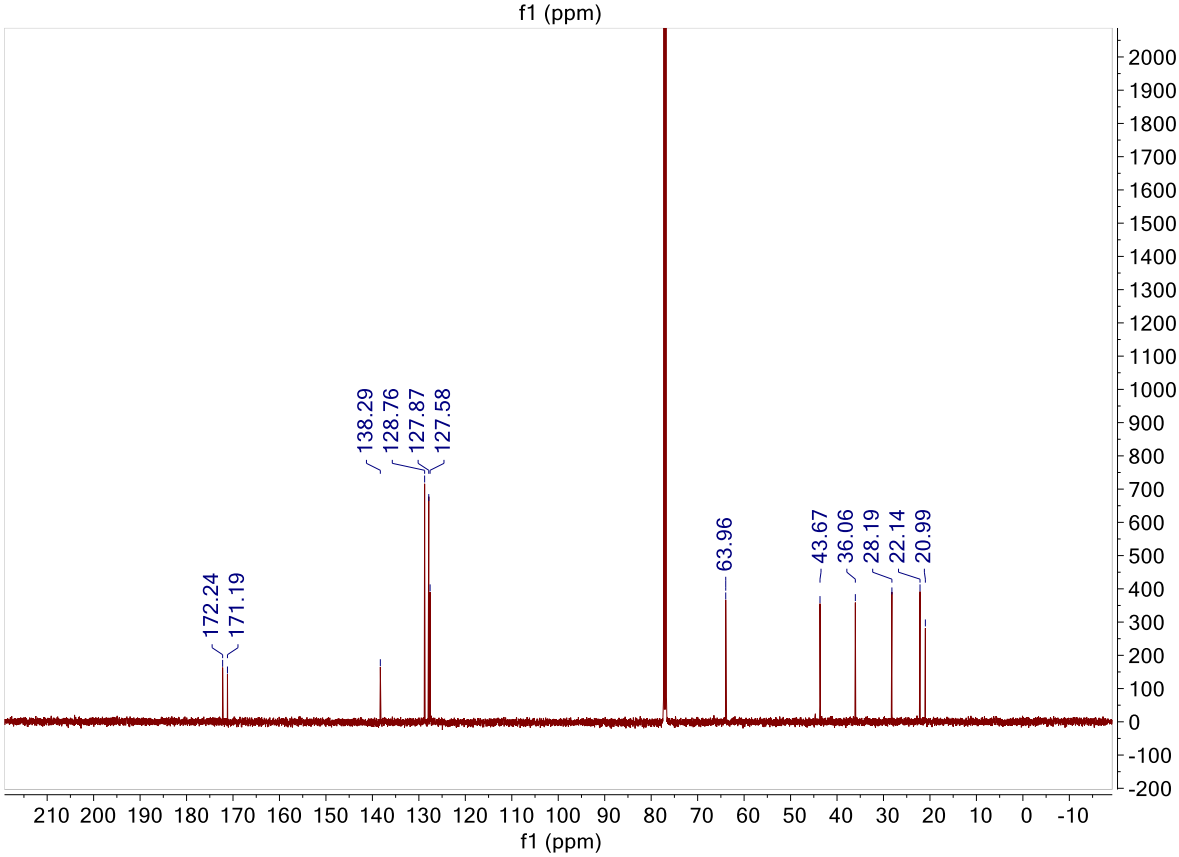




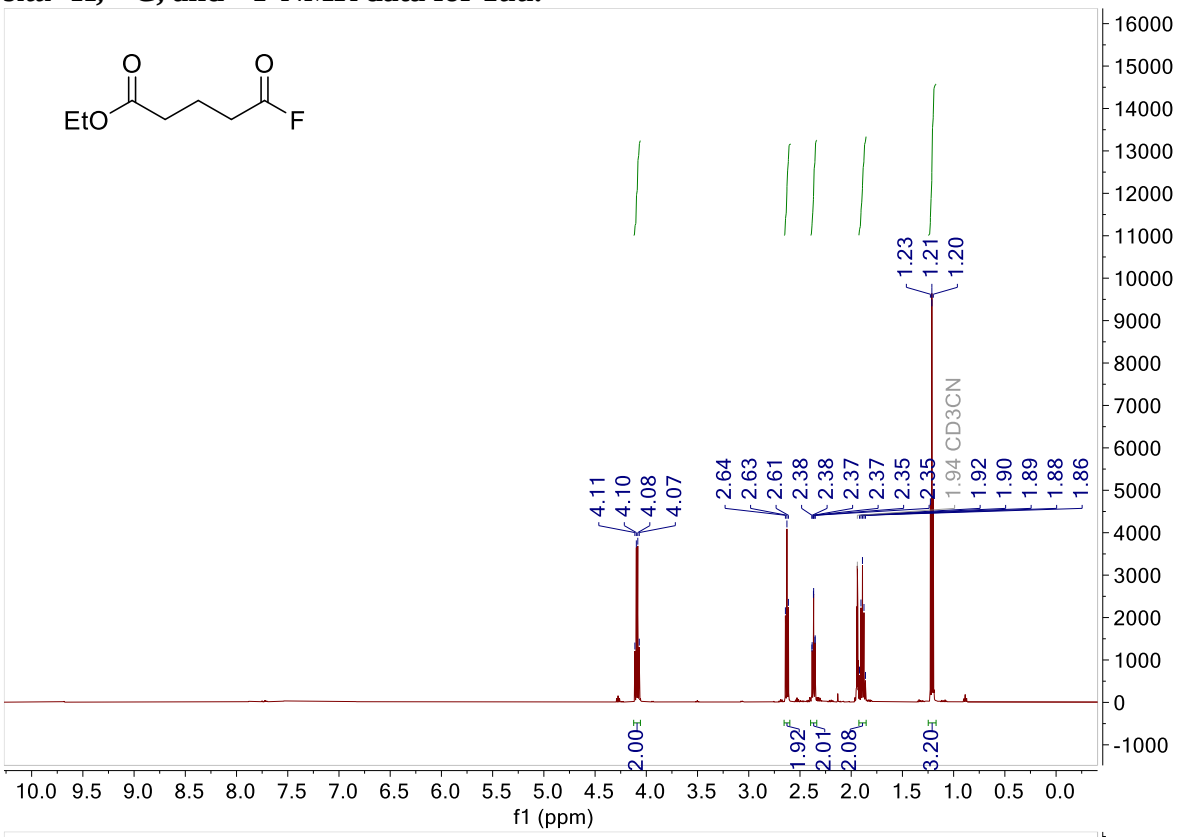

42.93
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
72 70 68 66 64 62 60 58 56 54 52 50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14
f1 (ppm)

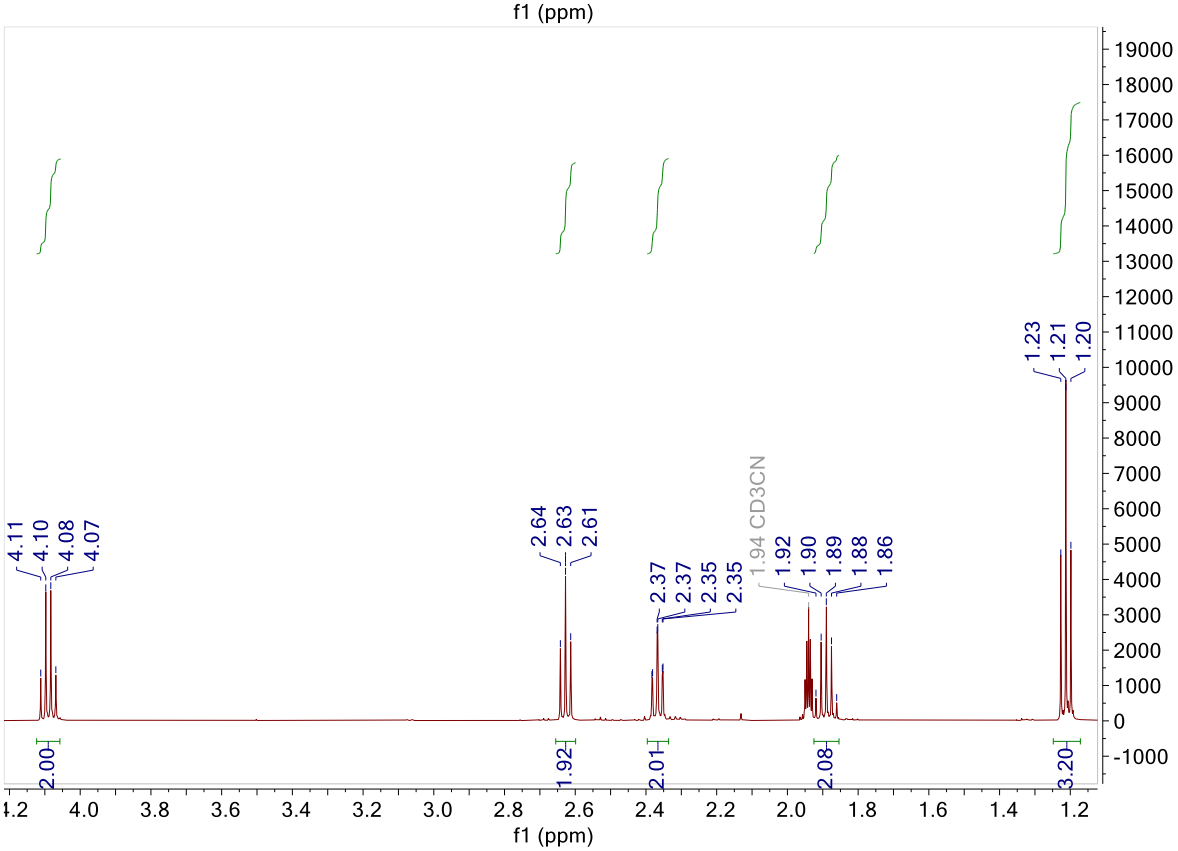
^{1}H and ^{13}C NMR data for 5tt.

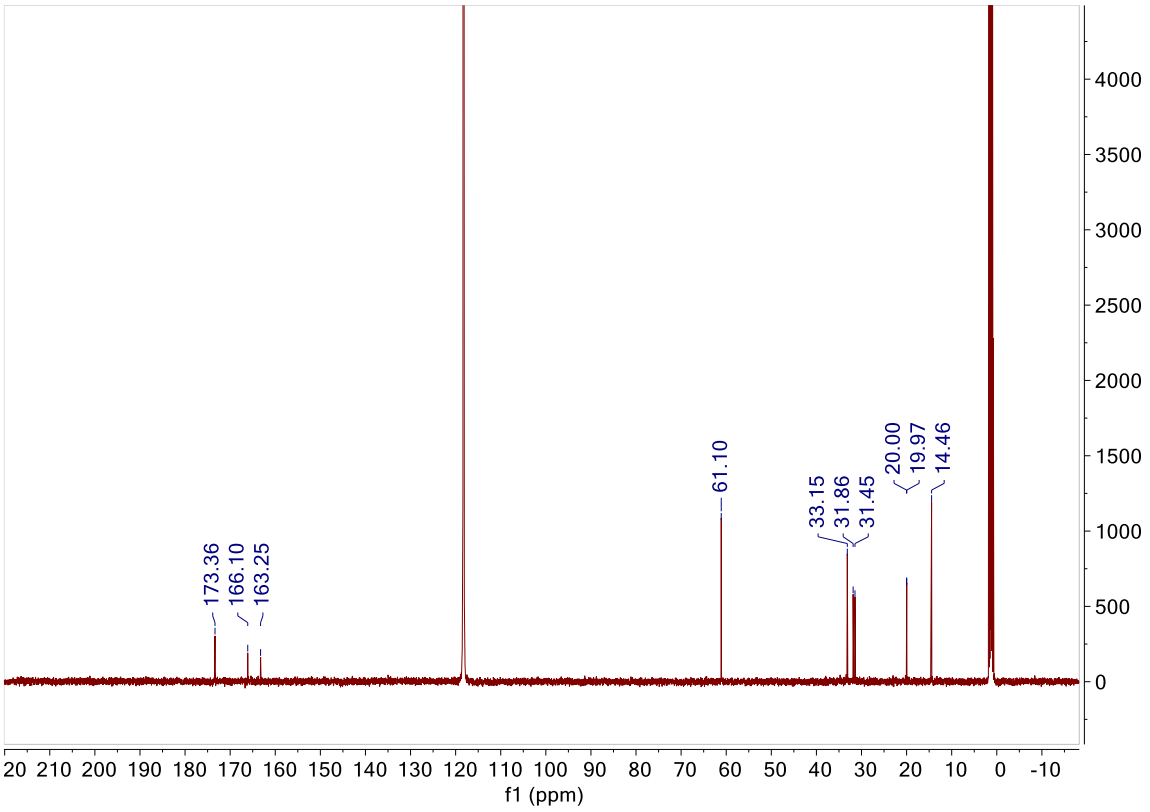


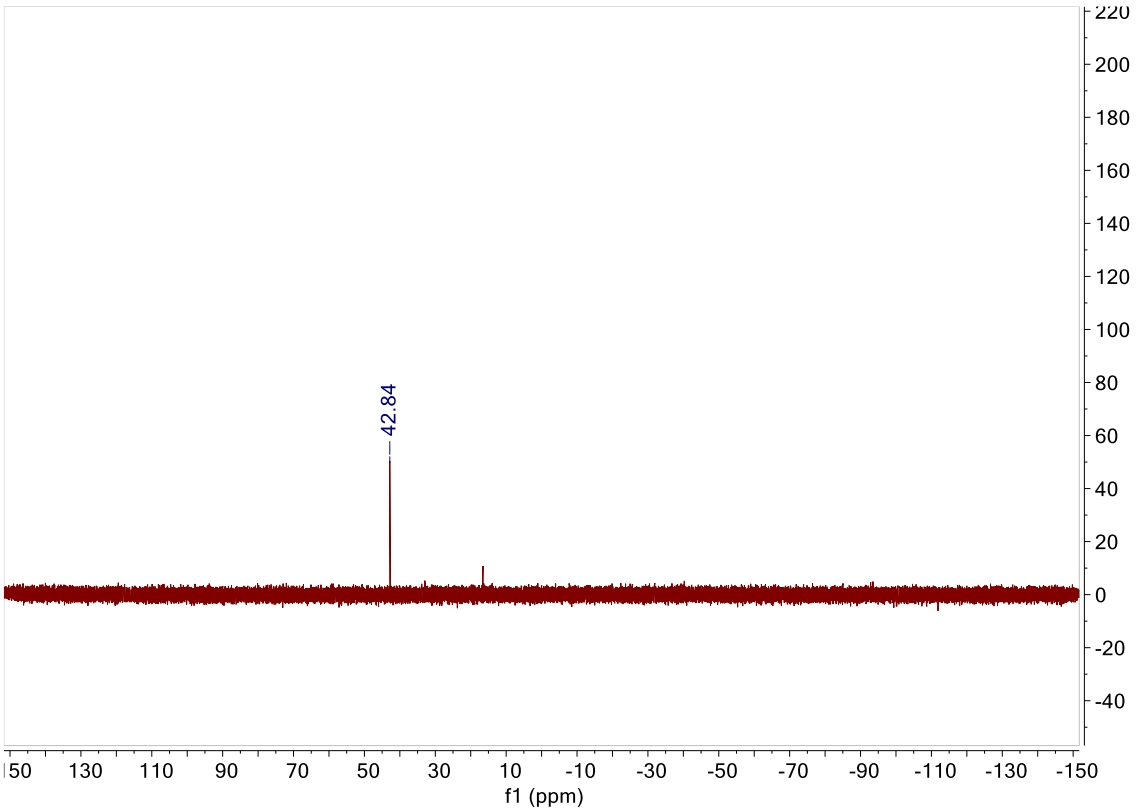


***In situ* ^{1}H, ^{13}C, and ^{19}F NMR data for 1uu.**

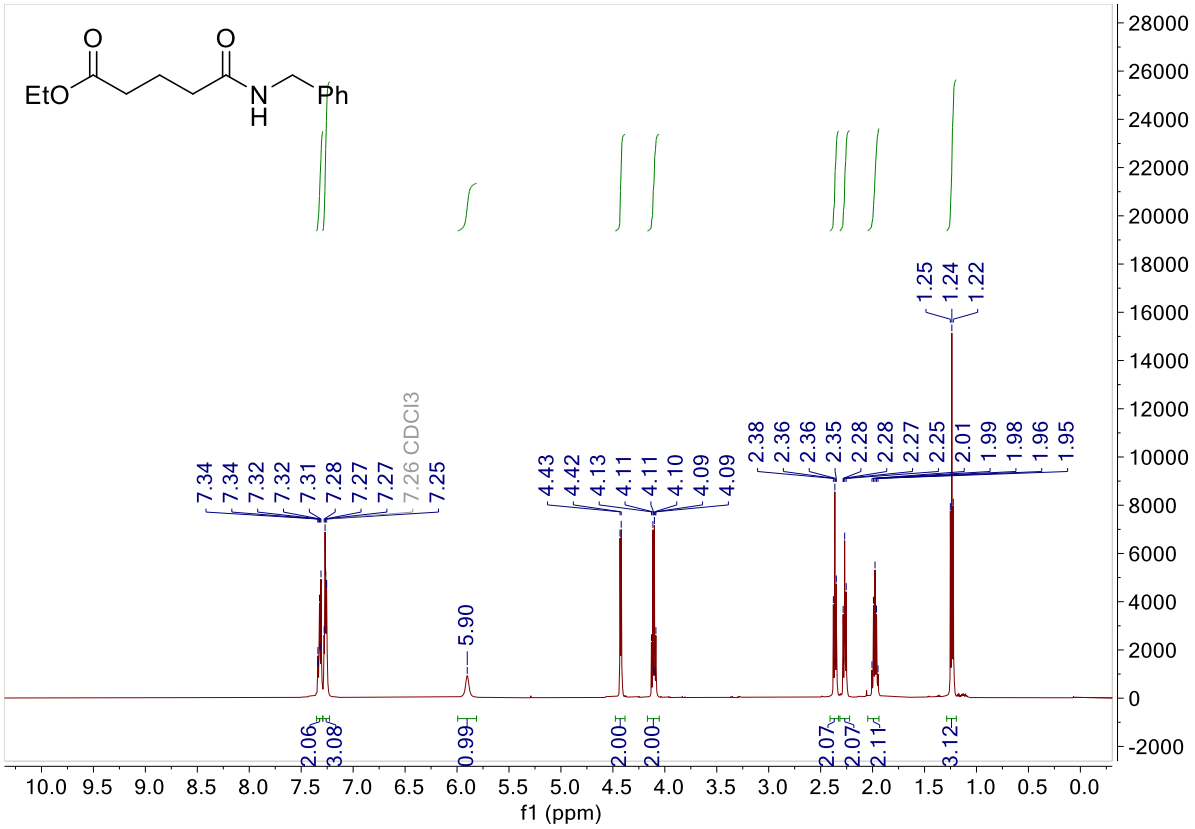


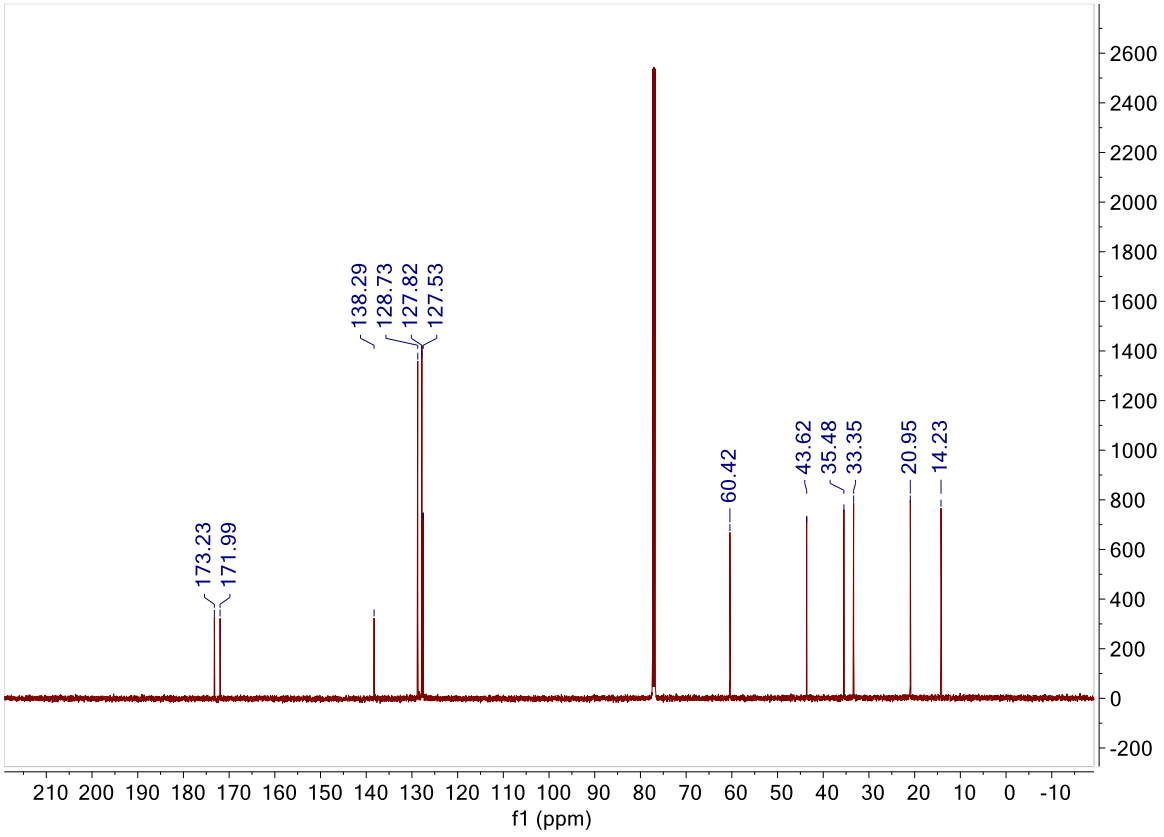



173.36
166.10
163.25
61.10
33.15
31.86
31.45
20.00
19.97
14.46
4000
3500
3000
2500
2000
1500
1000
500
0
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

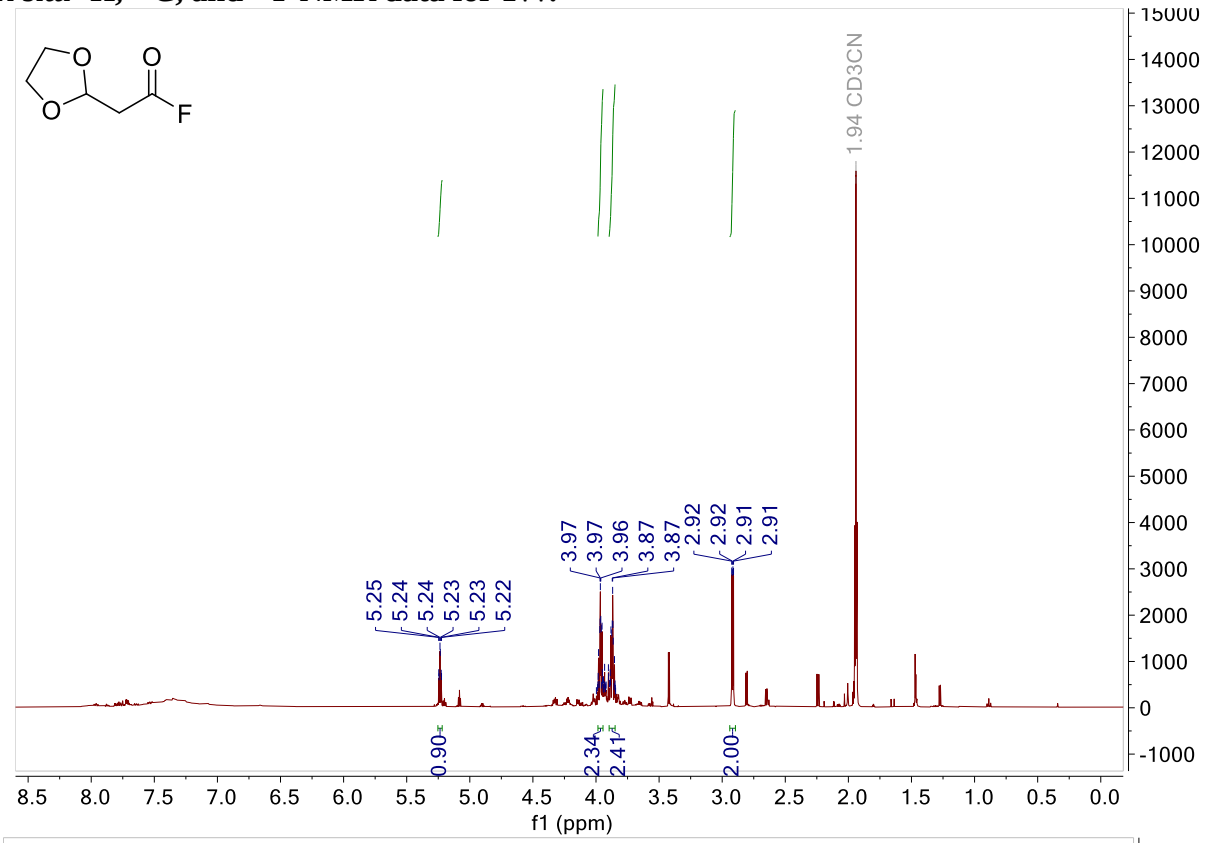

42.84
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
50 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150
f1 (ppm)

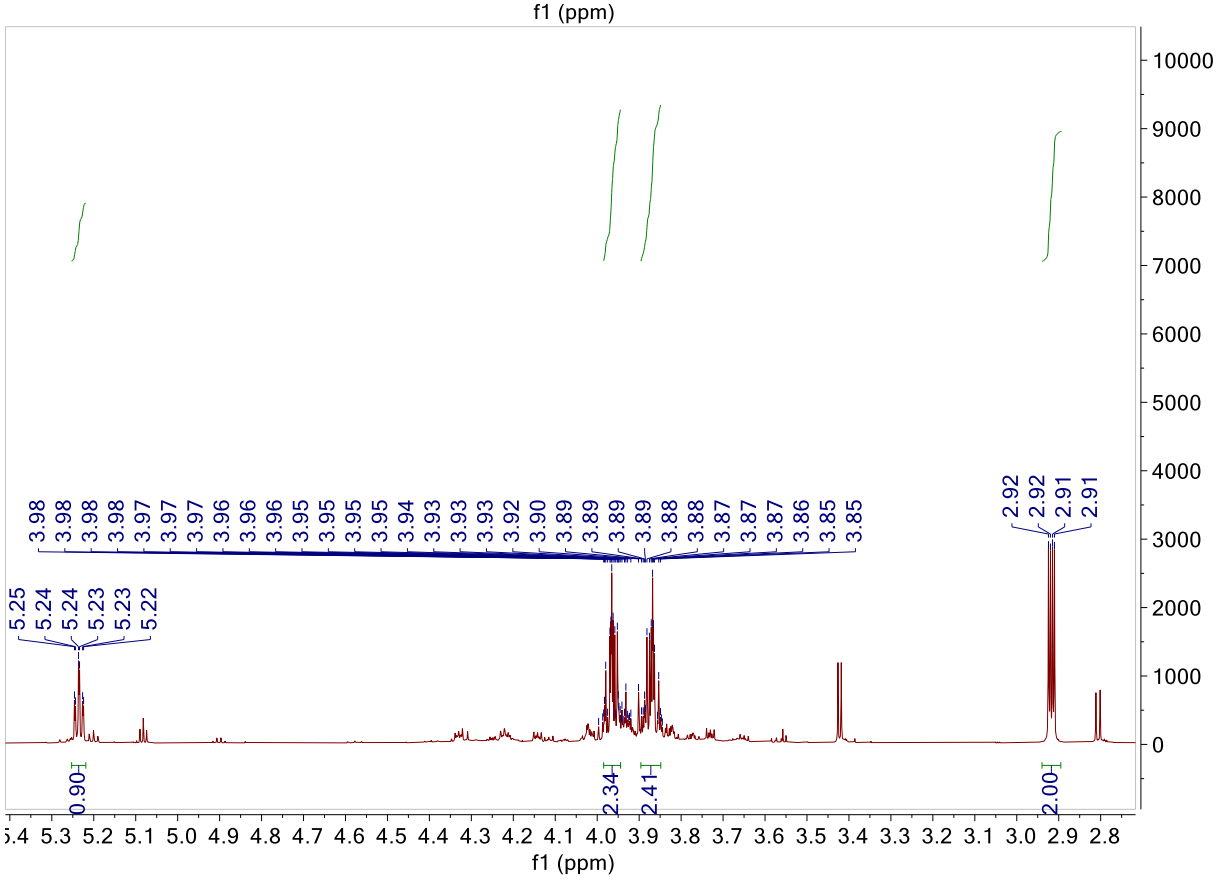
^{1}H and ^{13}C NMR data for 5uu.

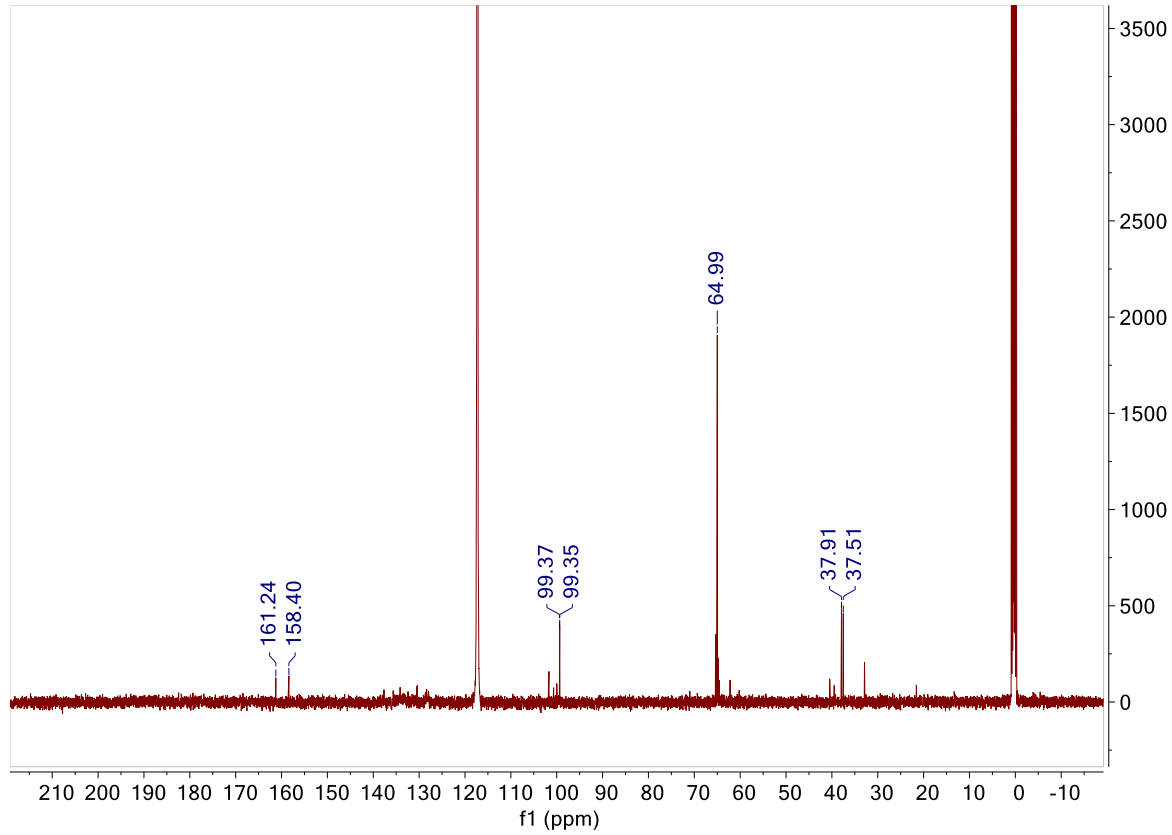


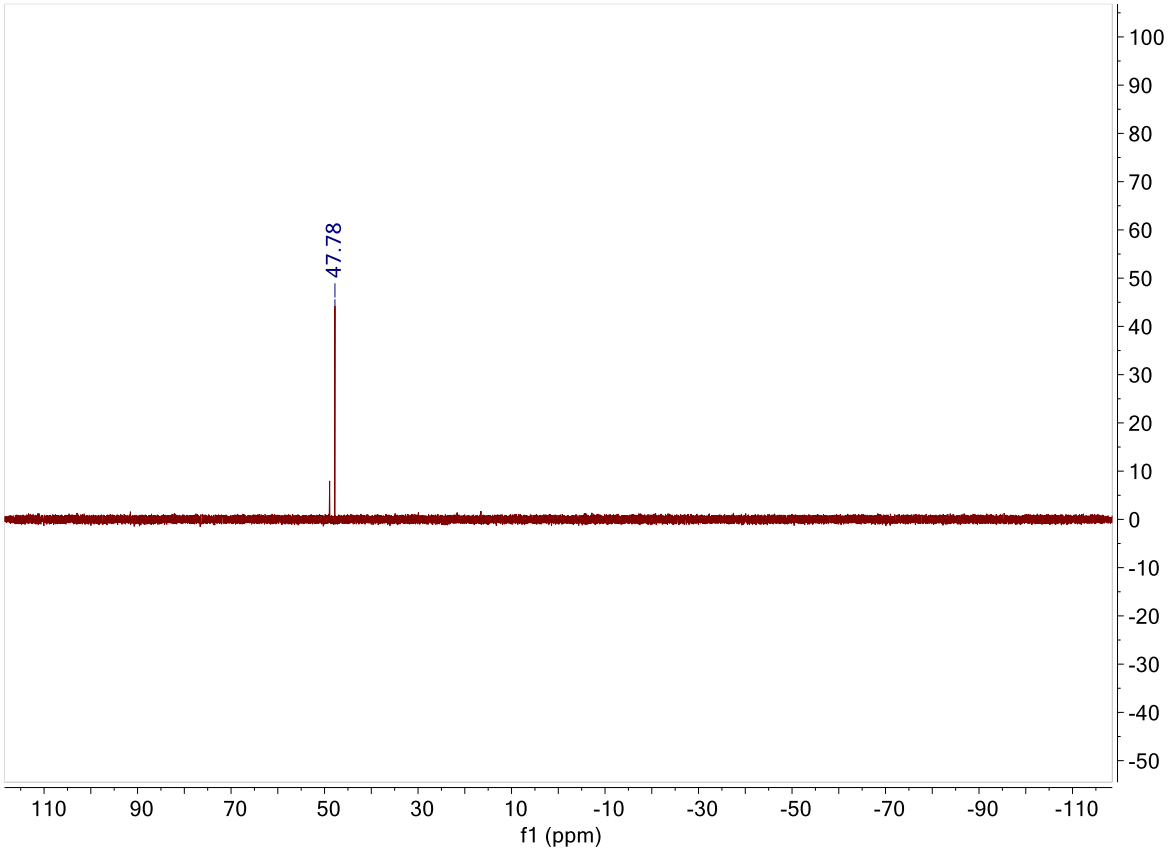


***In situ* ^{1}H, ^{13}C, and ^{19}F NMR data for 1vv.**

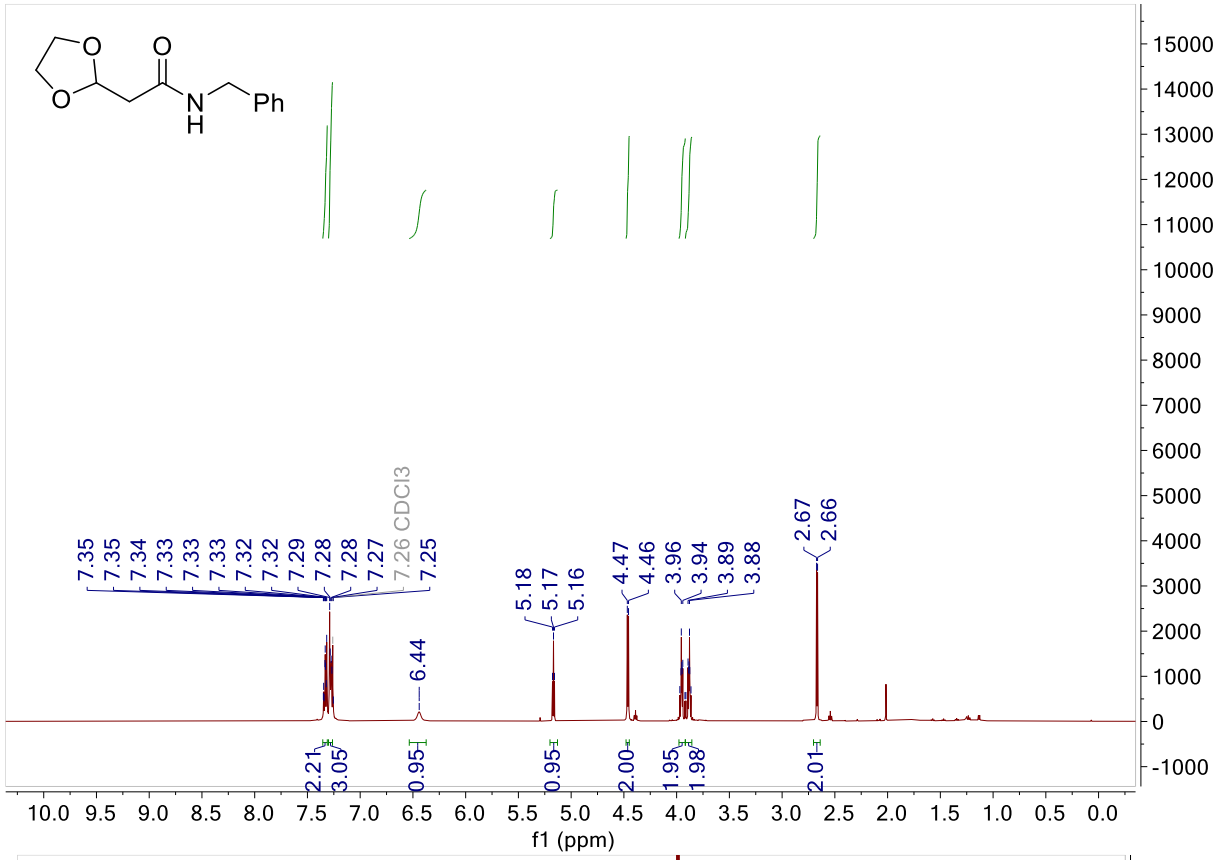


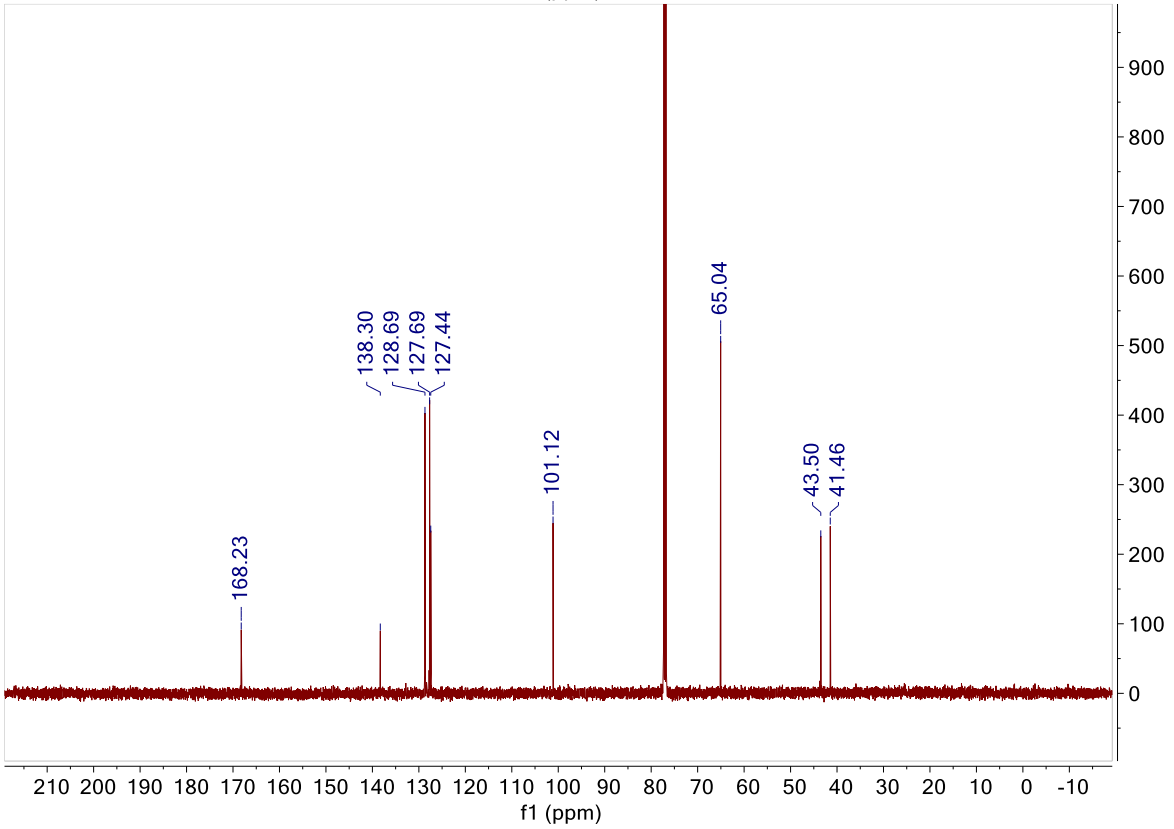



161.24
158.40
99.37
99.35
64.99
37.91
37.51
f1 (ppm)

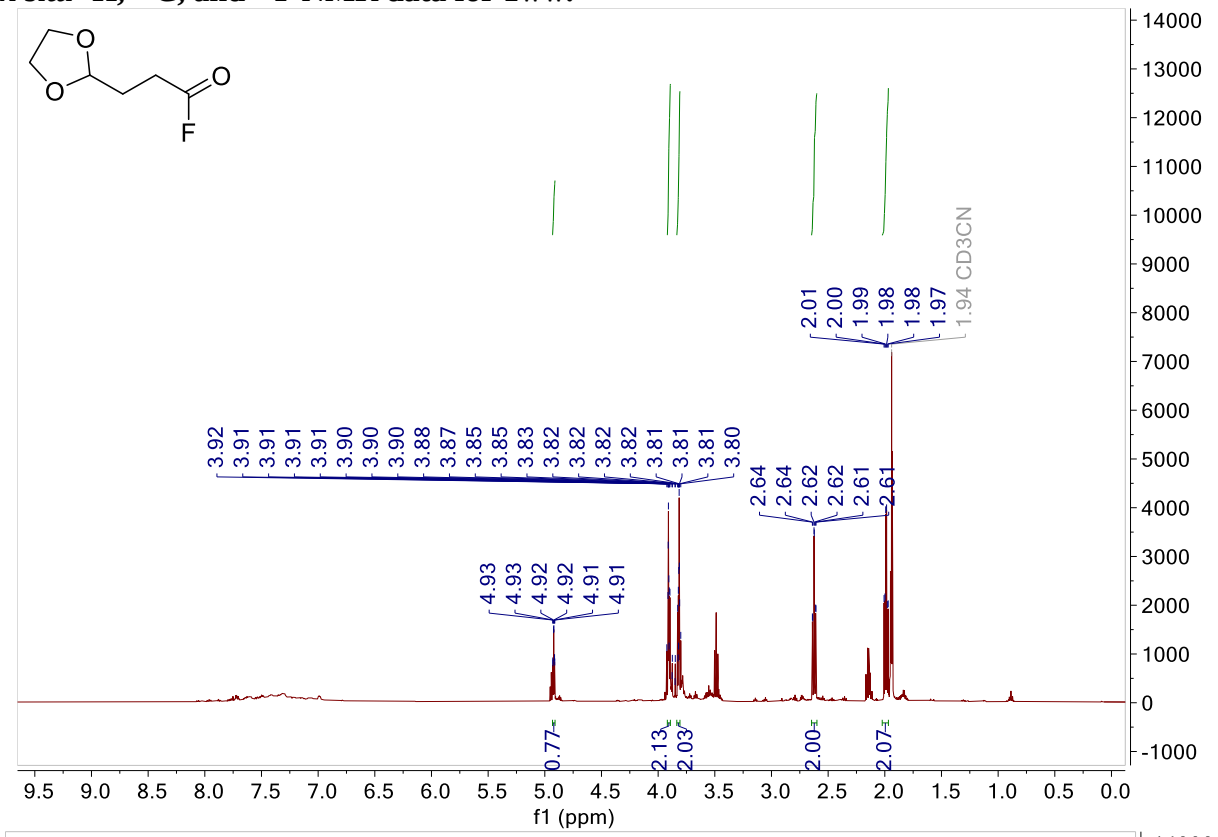

47.78
f1 (ppm)

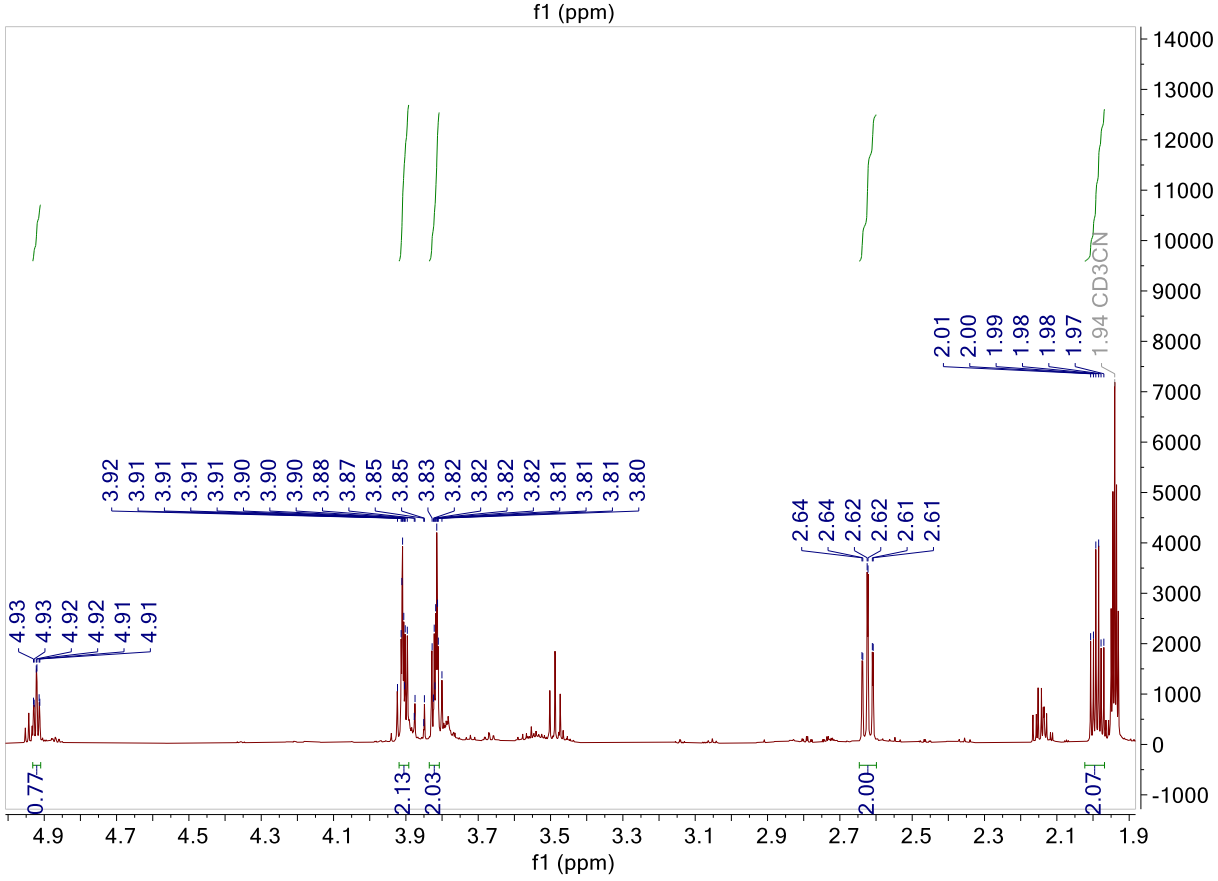
^{1}H and ^{13}C NMR data for 5vv.

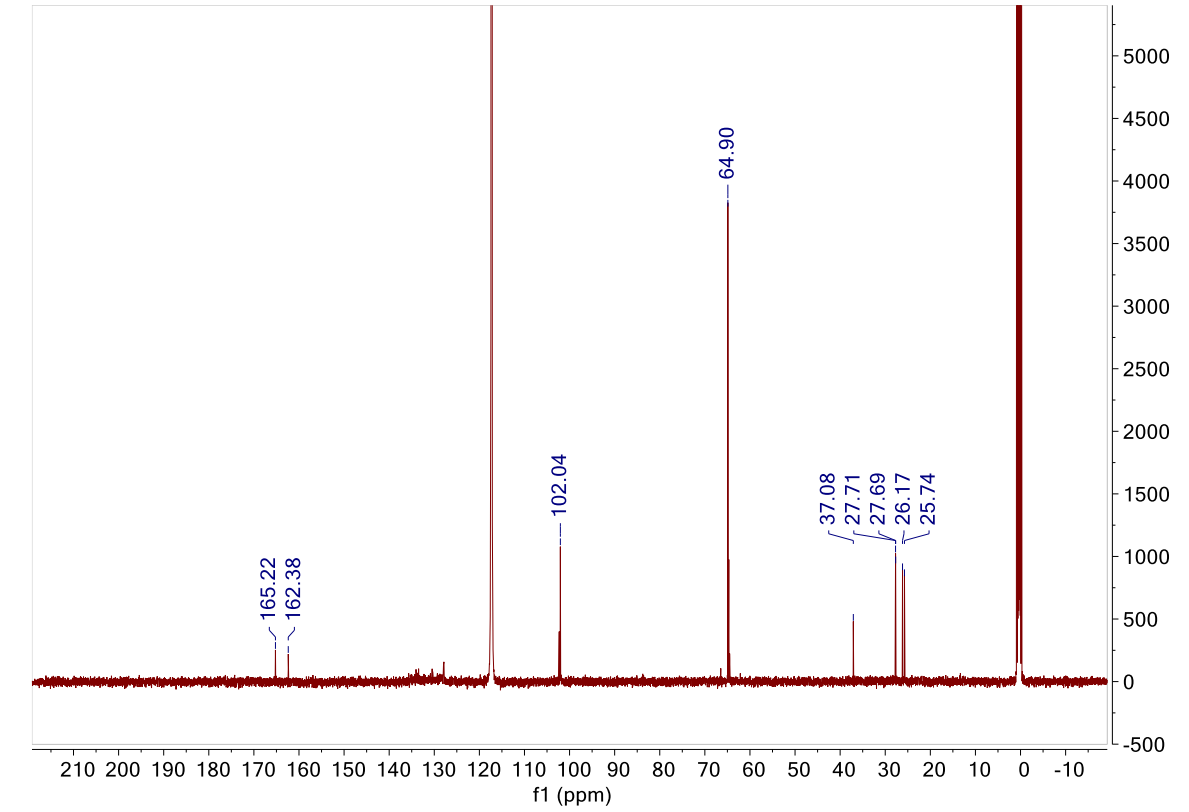


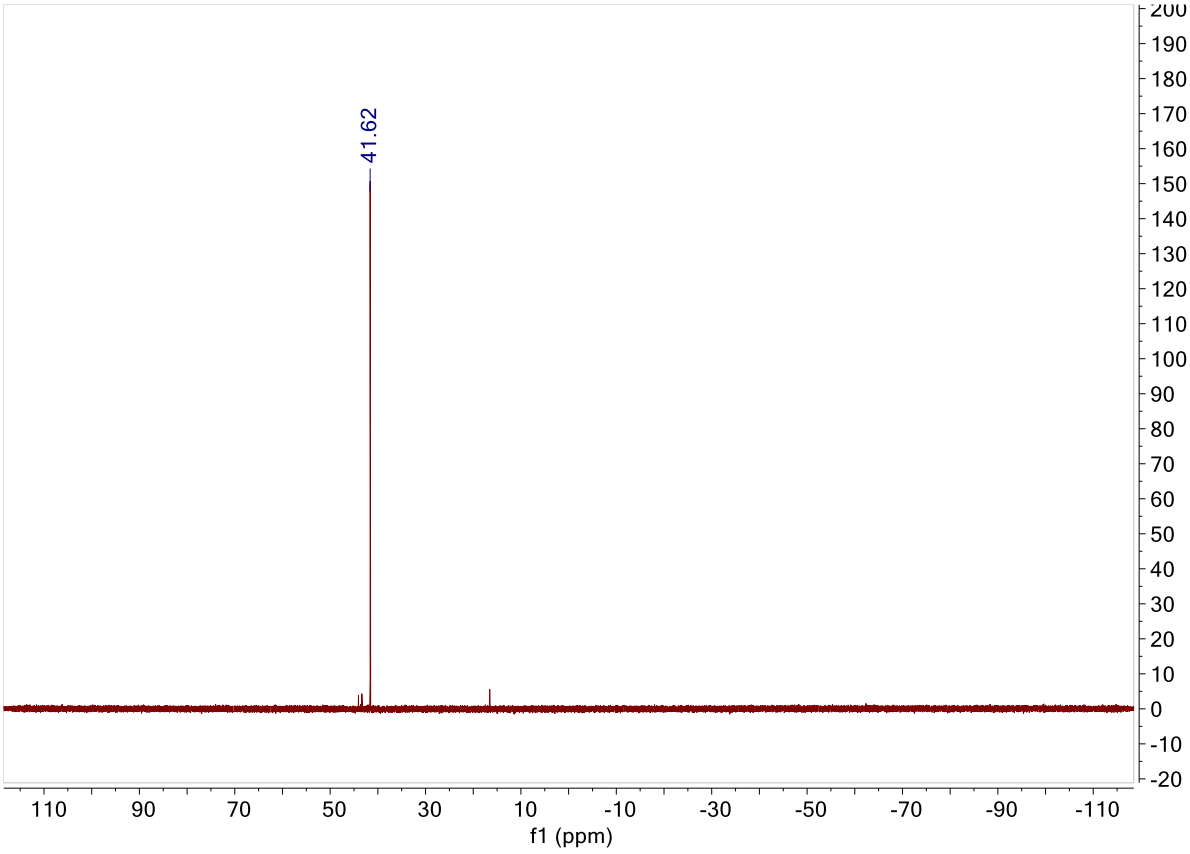


***In situ* ^{1}H, ^{13}C, and ^{19}F NMR data for 1ww.**

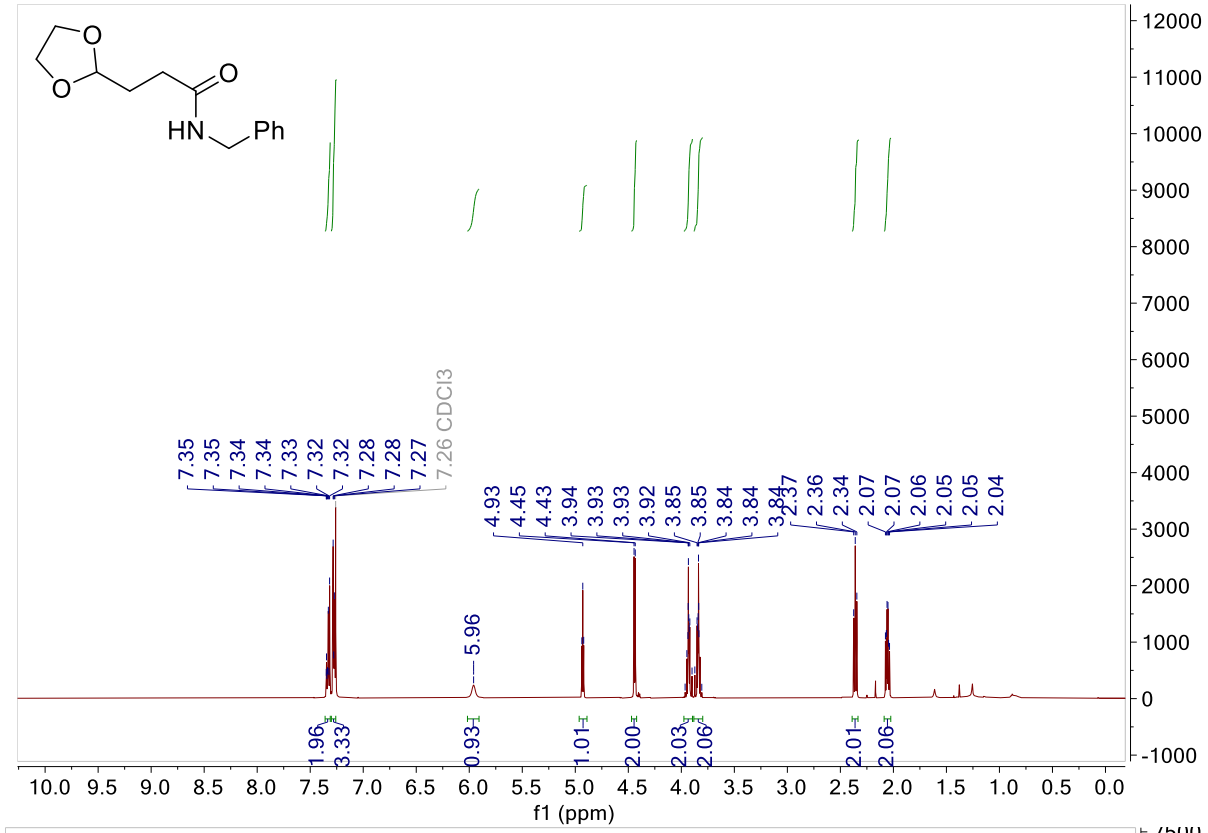


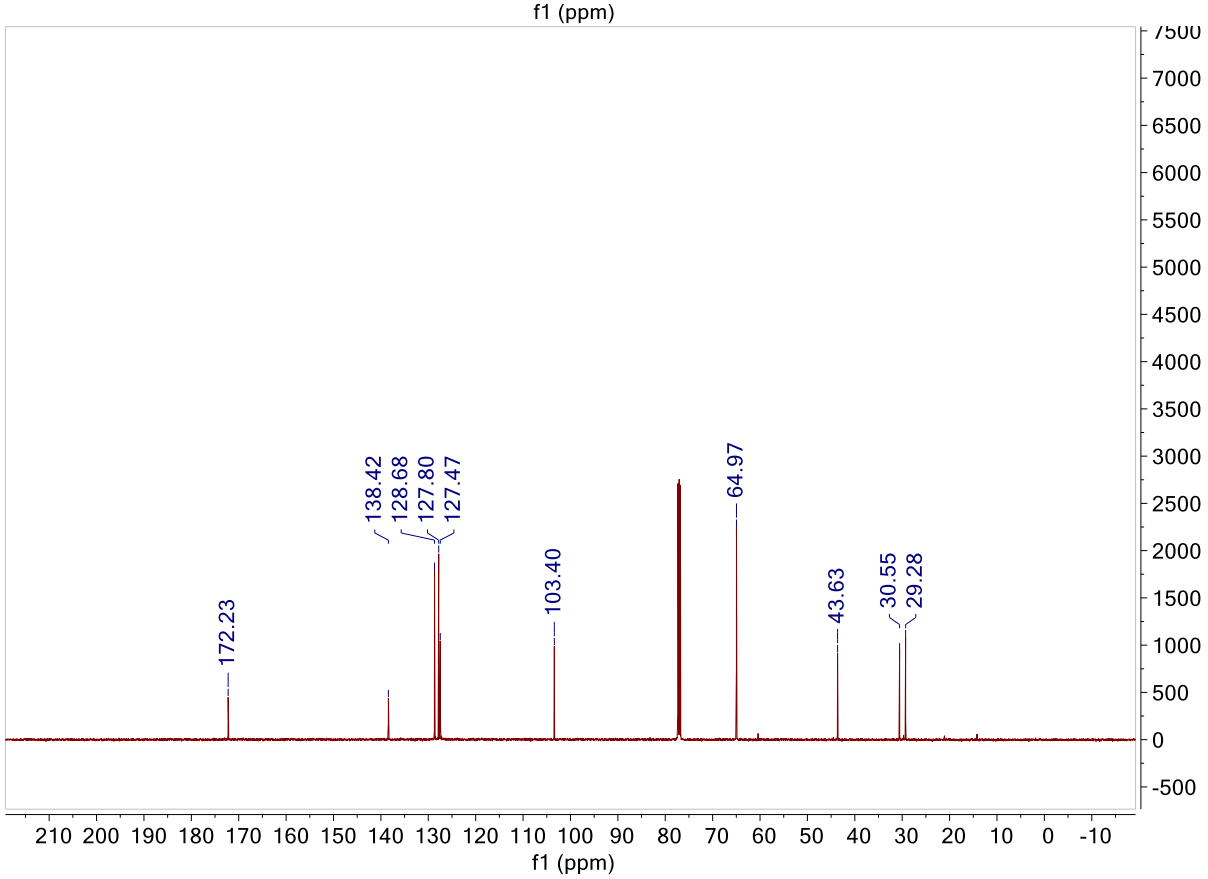



165.22
162.38
102.04
64.90
37.08
27.71
27.69
26.17
25.74
f1 (ppm)

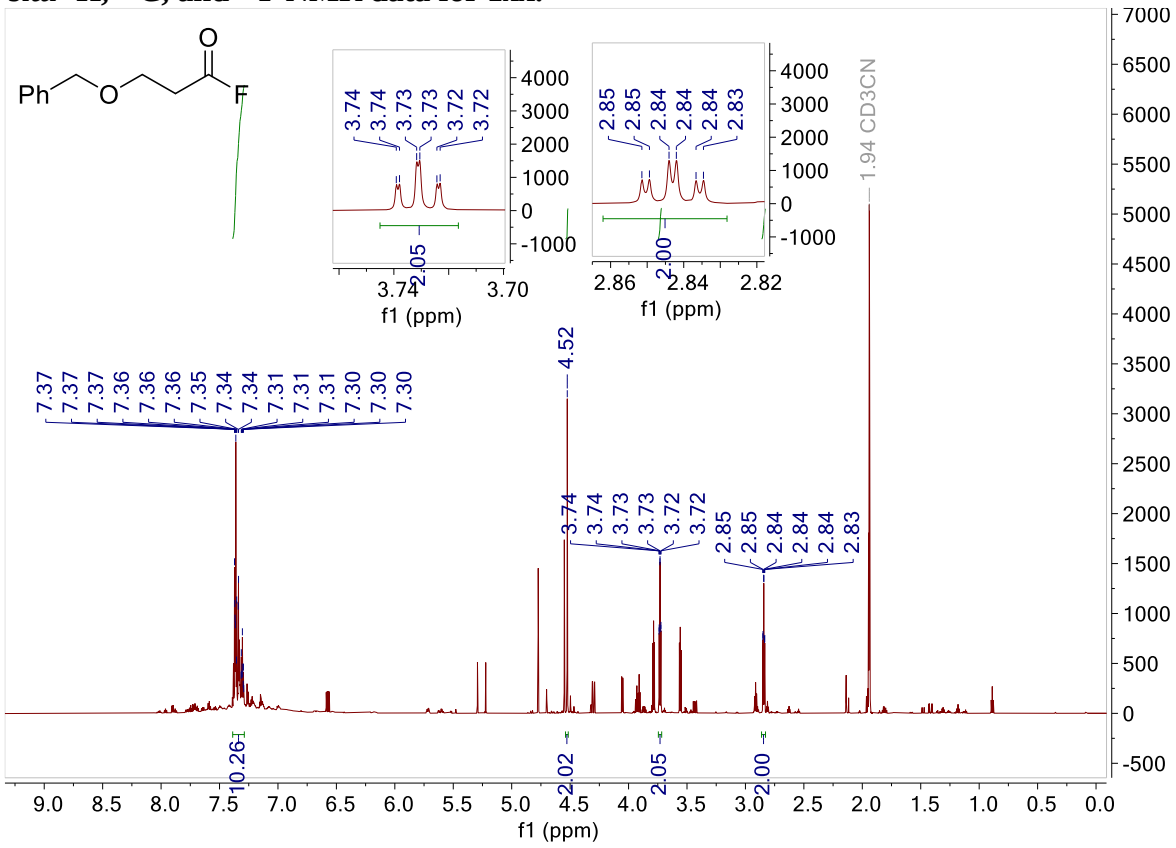

41.62
f1 (ppm)

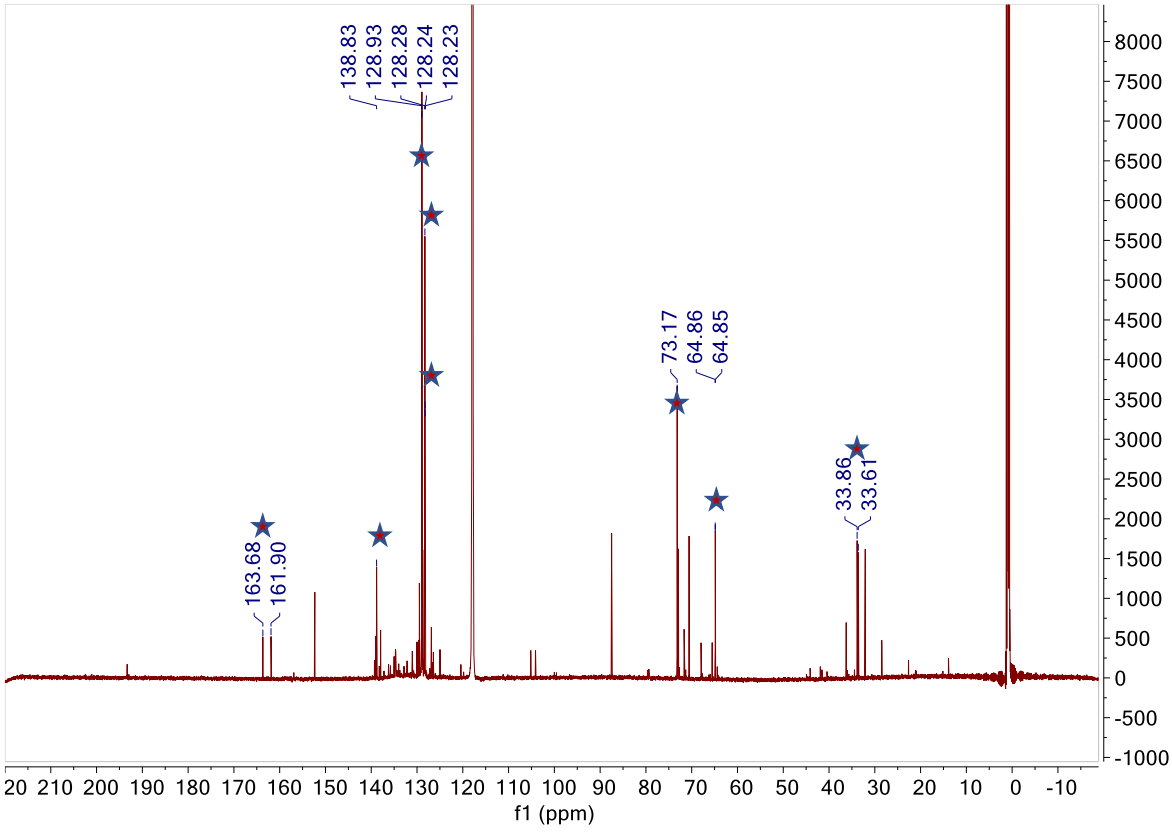
^{1}H and ^{13}C NMR data for 5ww.

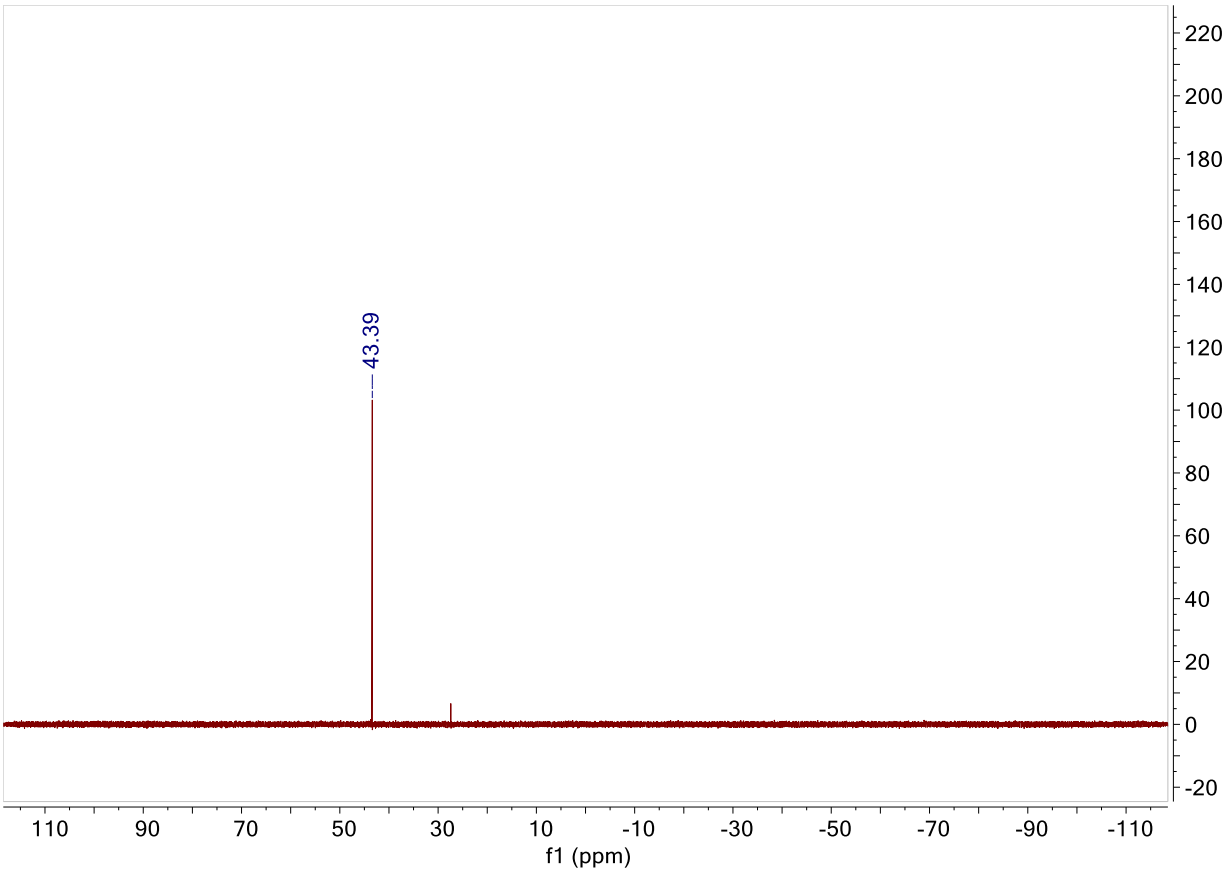




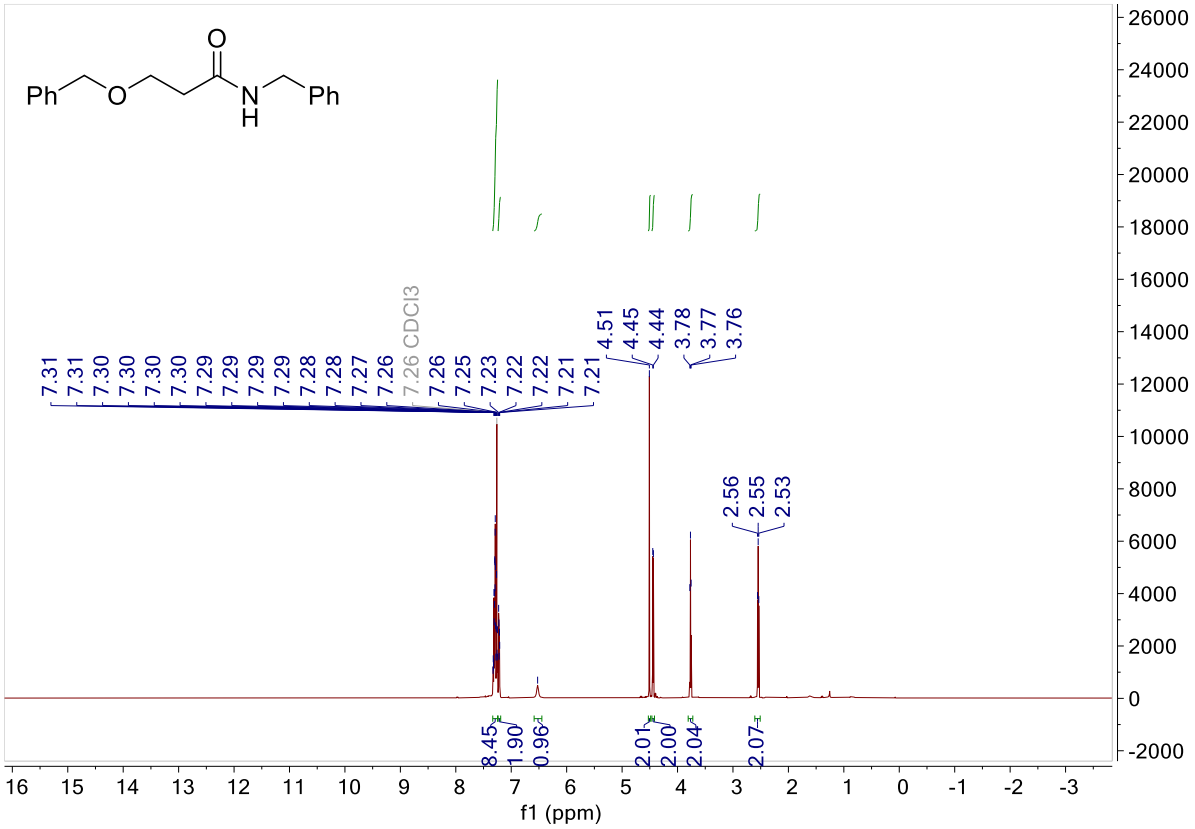
***In situ* ^{1}H, ^{13}C, and ^{19}F NMR data for 1xx.**

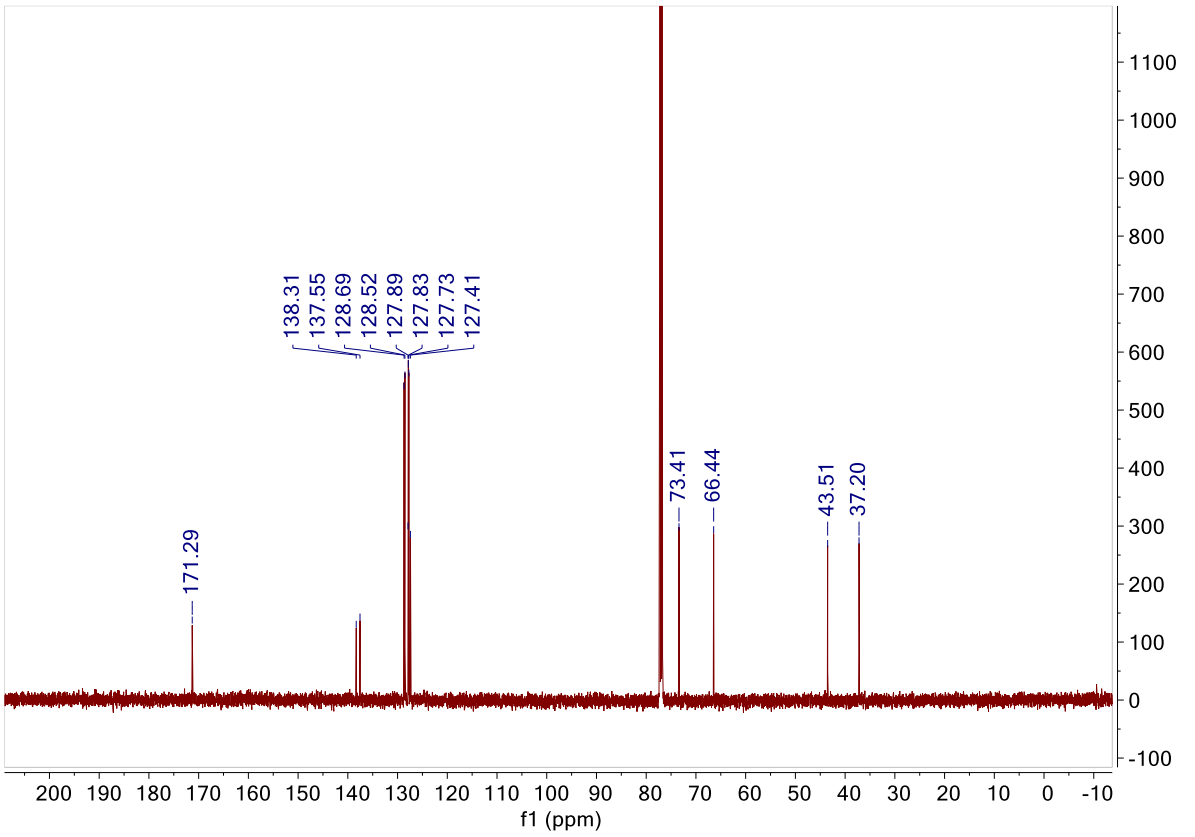




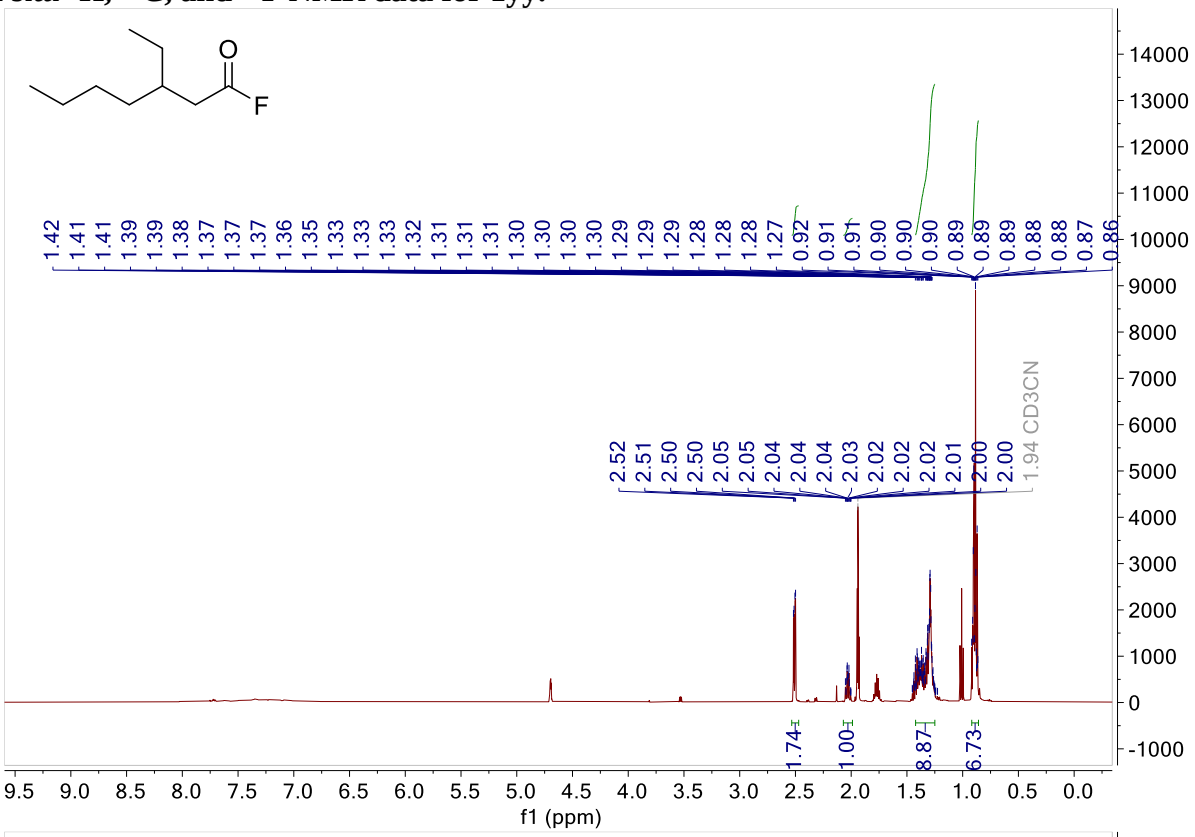

43.39
220
200
180
160
140
120
100
80
60
40
20
0
-20
110
90
70
50
30
10
-10
-30
-50
-70
-90
-110
f1 (ppm)

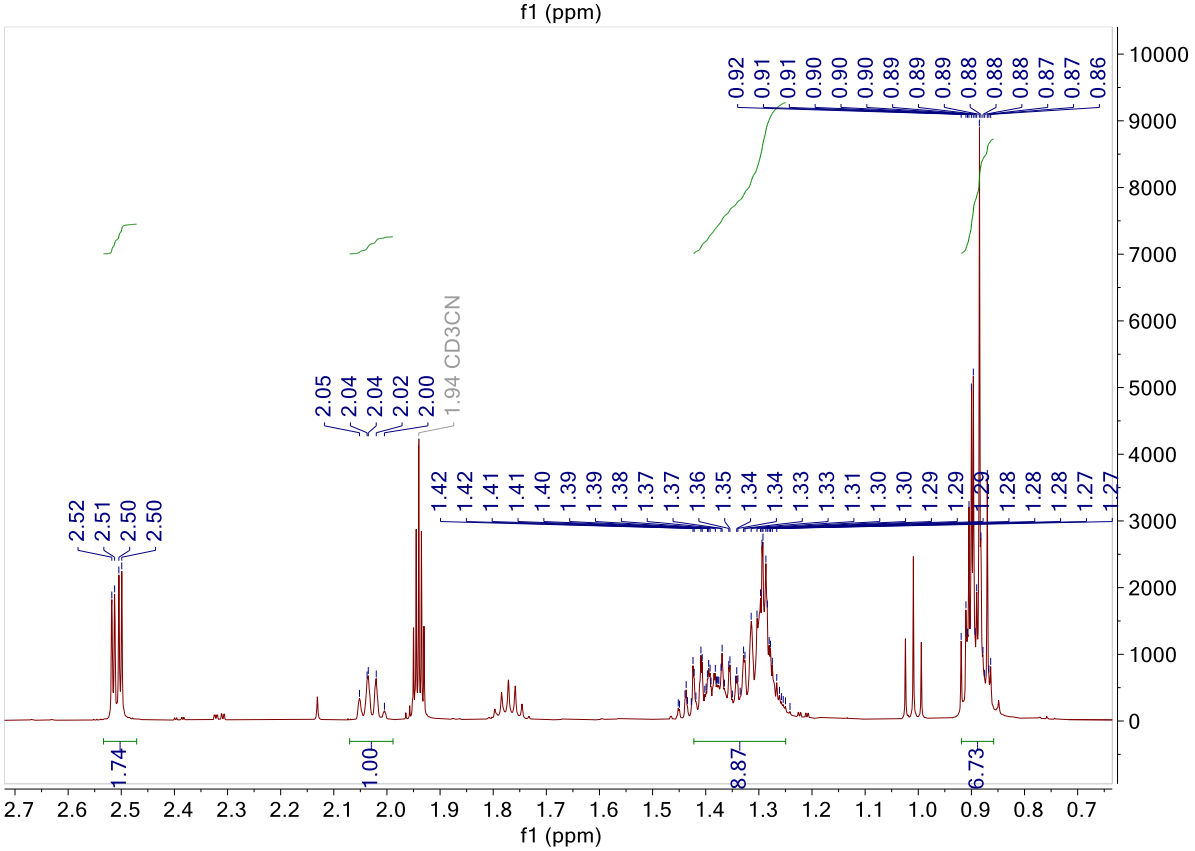
^{1}H and ^{13}C NMR data for 5xx.

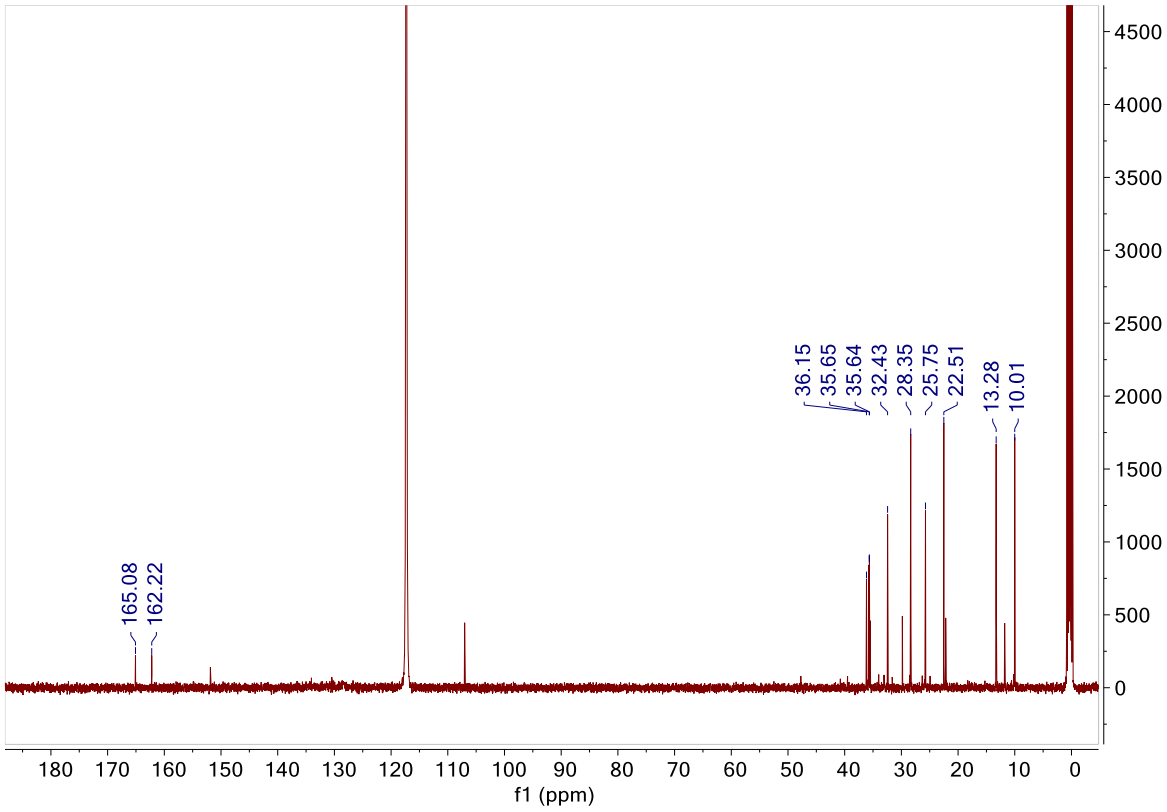


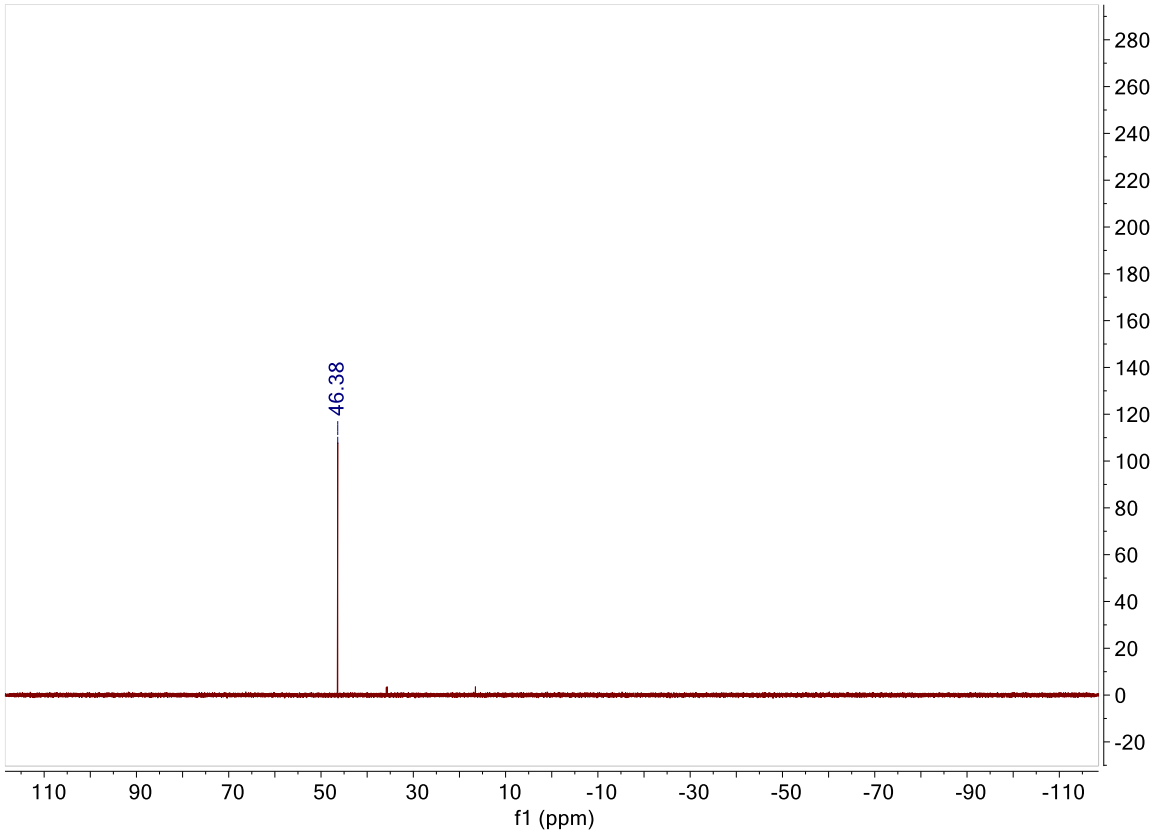


***In situ* ^{1}H, ^{13}C, and ^{19}F NMR data for 1yy.**

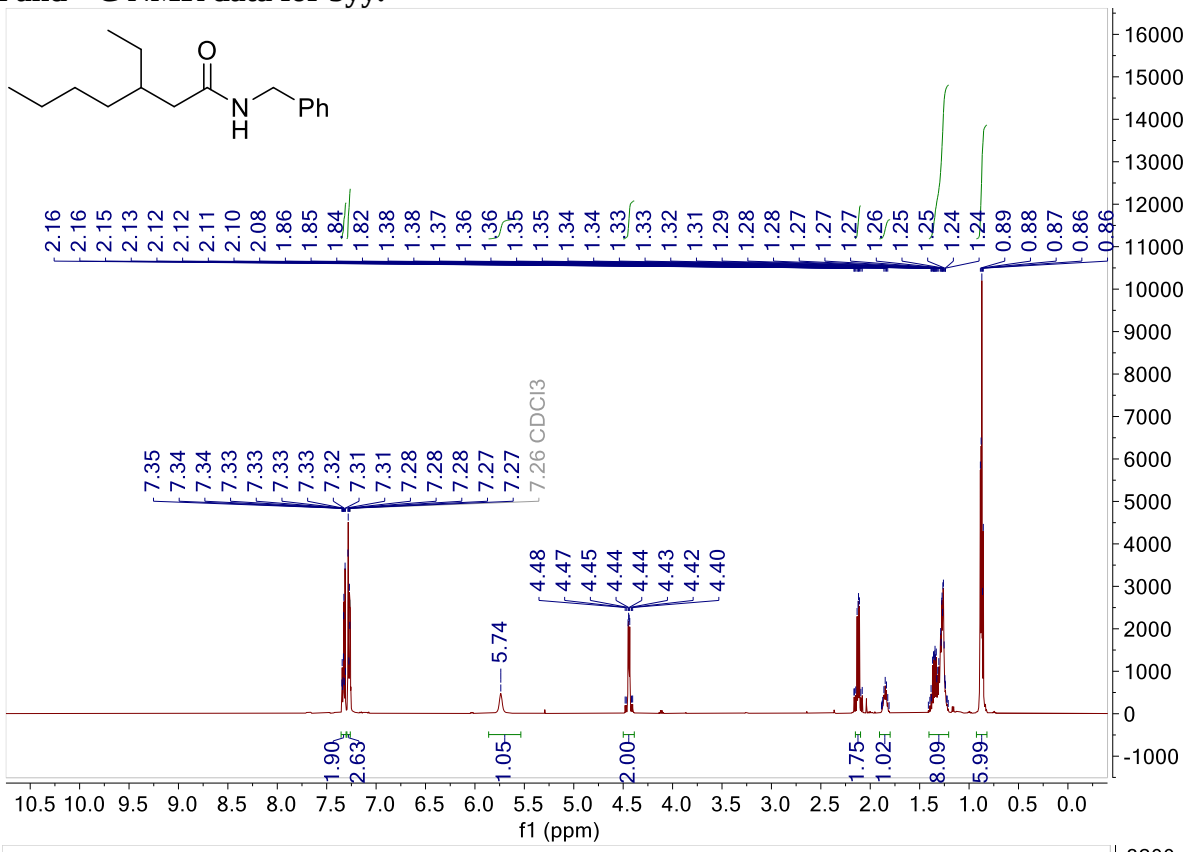


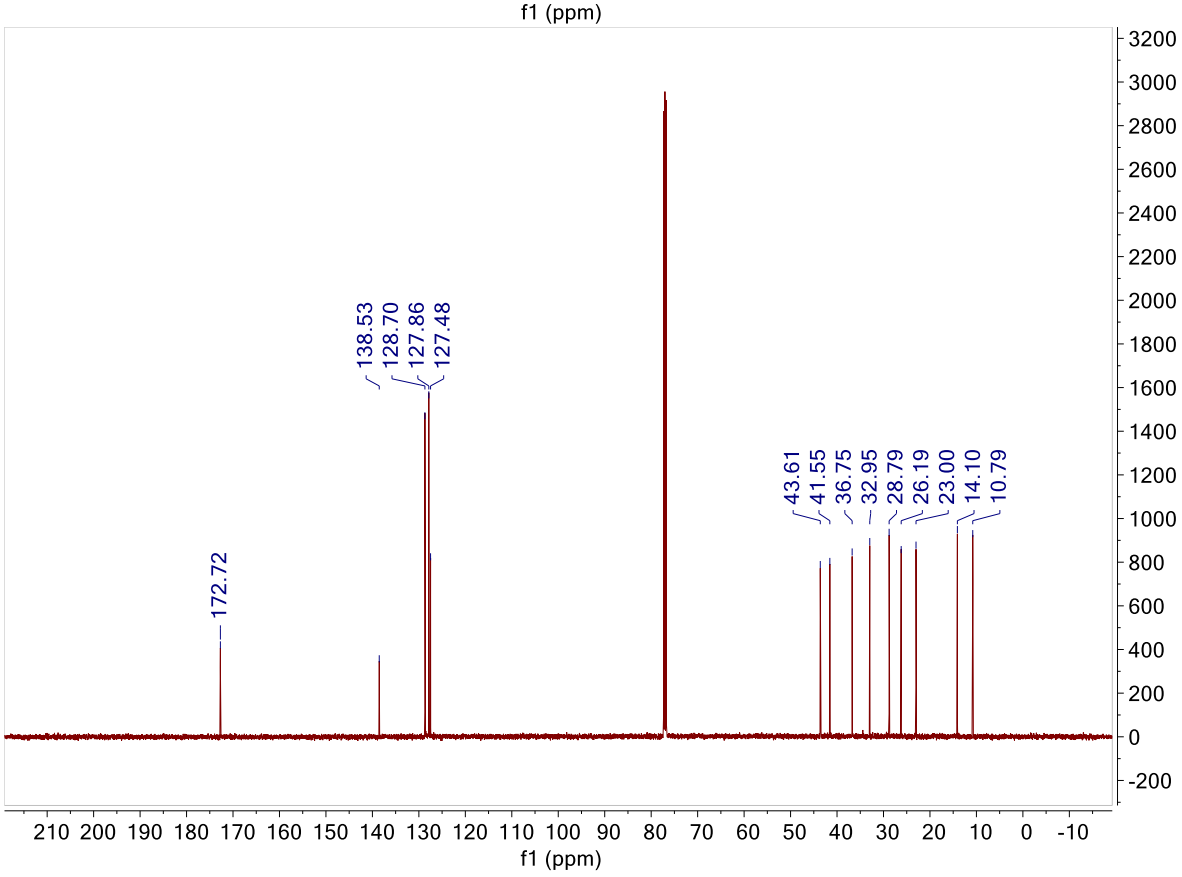



165.08
162.22
36.15
35.65
35.64
32.43
28.35
25.75
22.51
13.28
10.01
f1 (ppm)

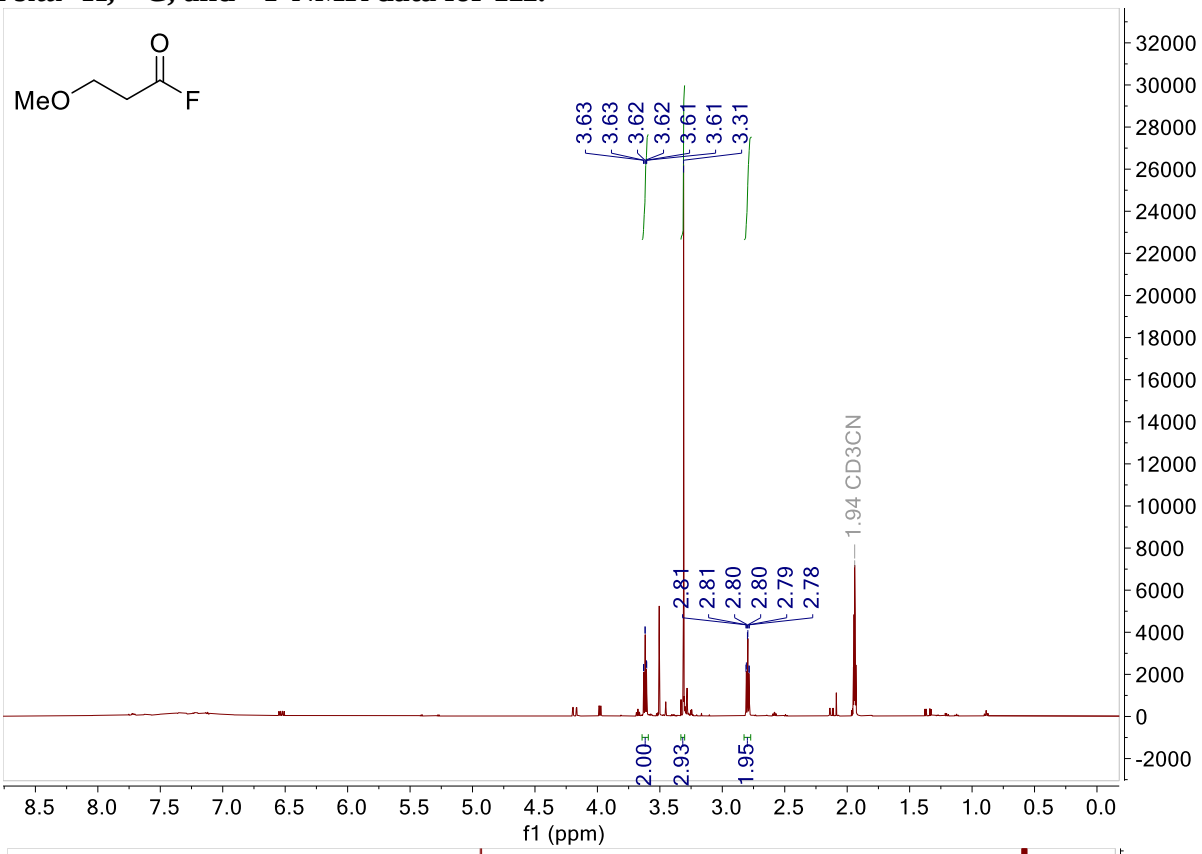

46.38
f1 (ppm)

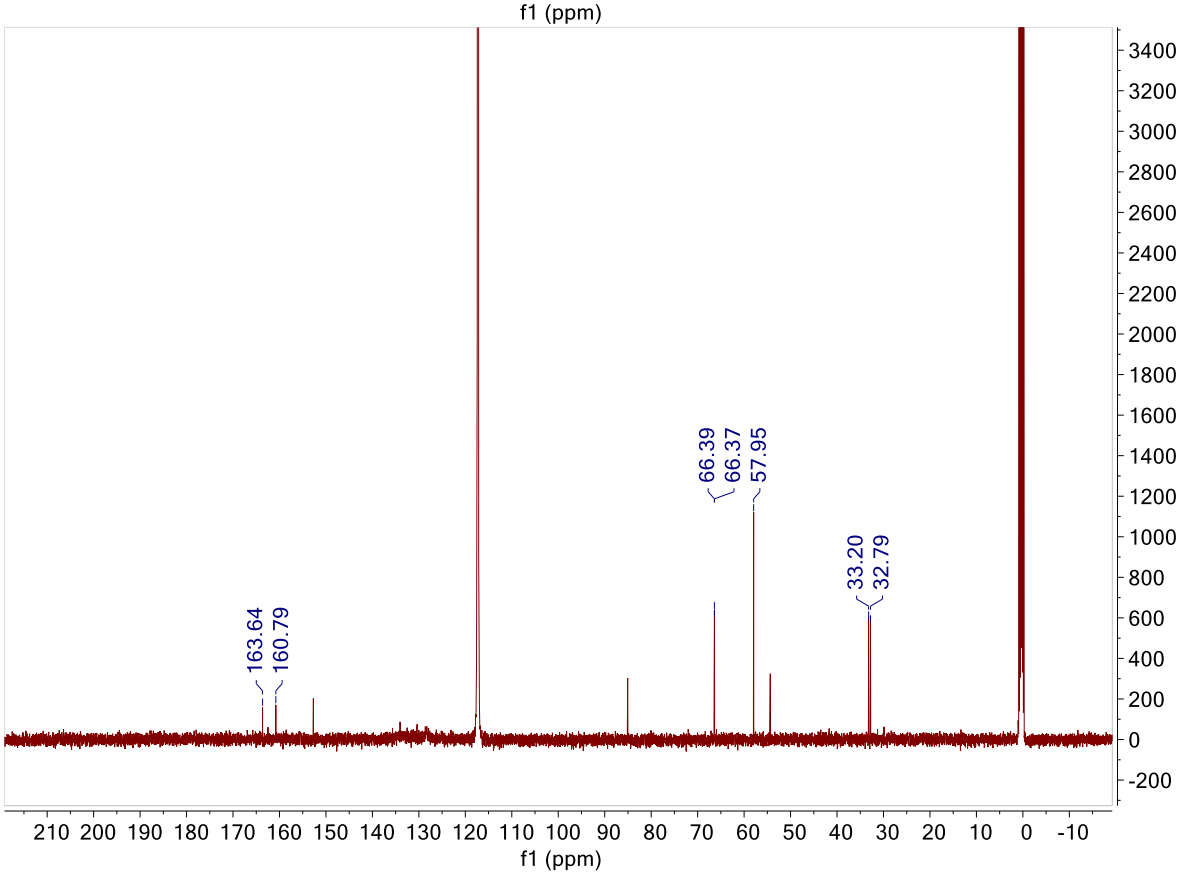
^{1}H and ^{13}C NMR data for 5yy.

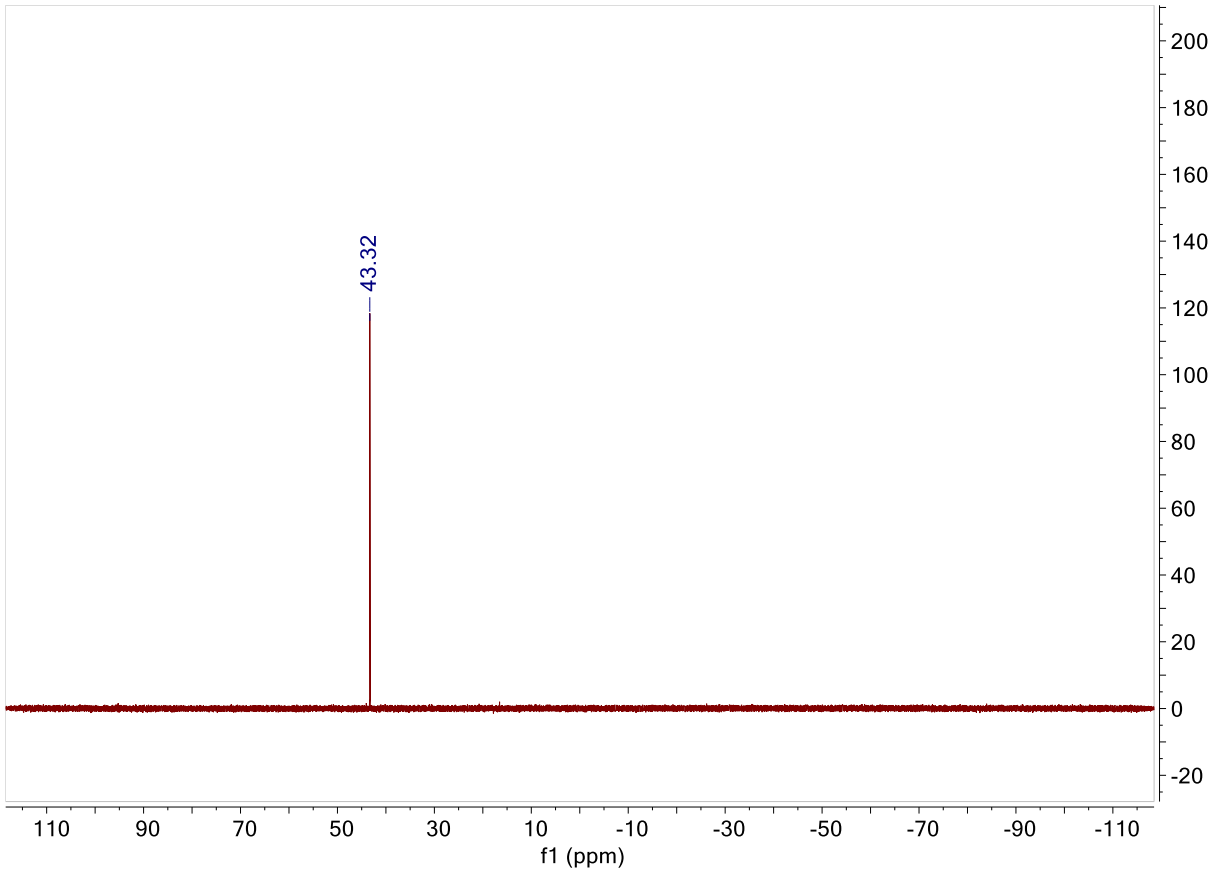




***In situ* ^{1}H, ^{13}C, and ^{19}F NMR data for 1zz.**






43.32
200
180
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140
120
100
80
60
40
20
0
-20
110
90
70
50
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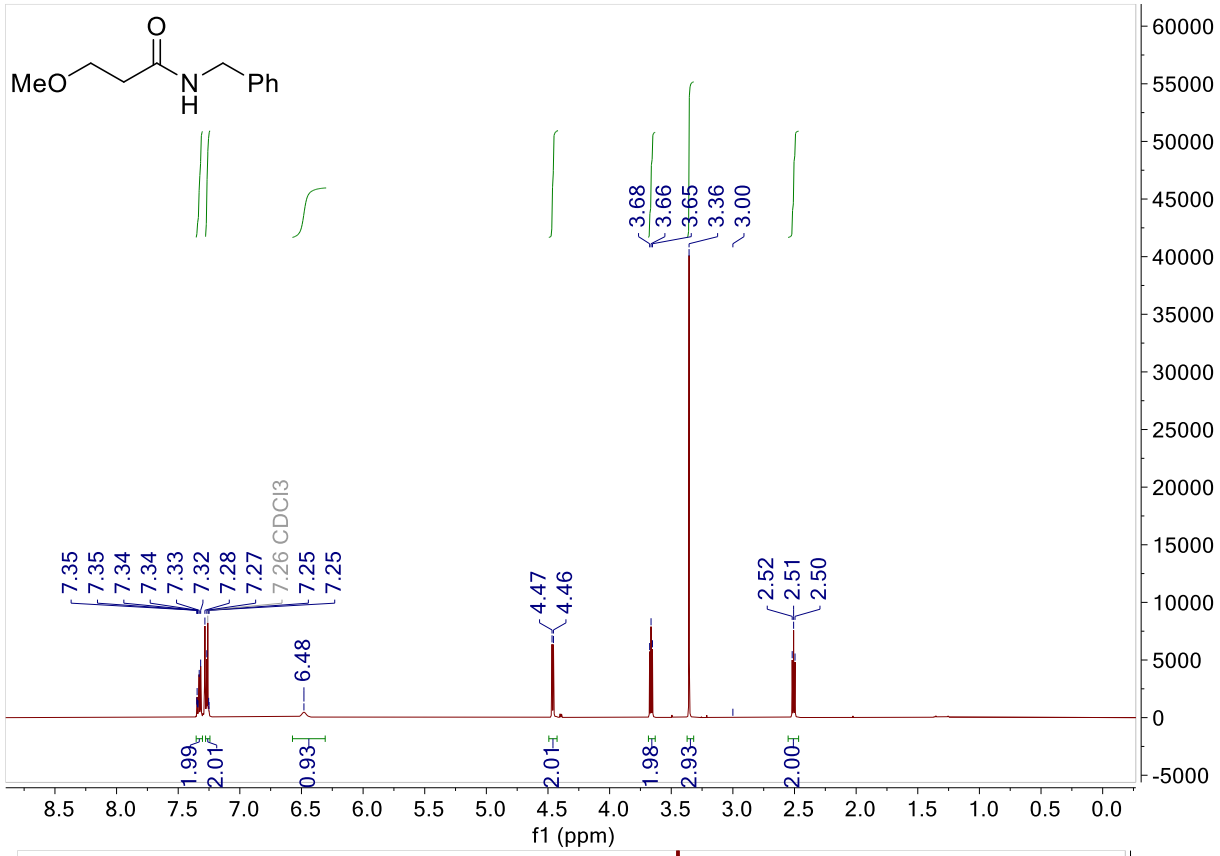
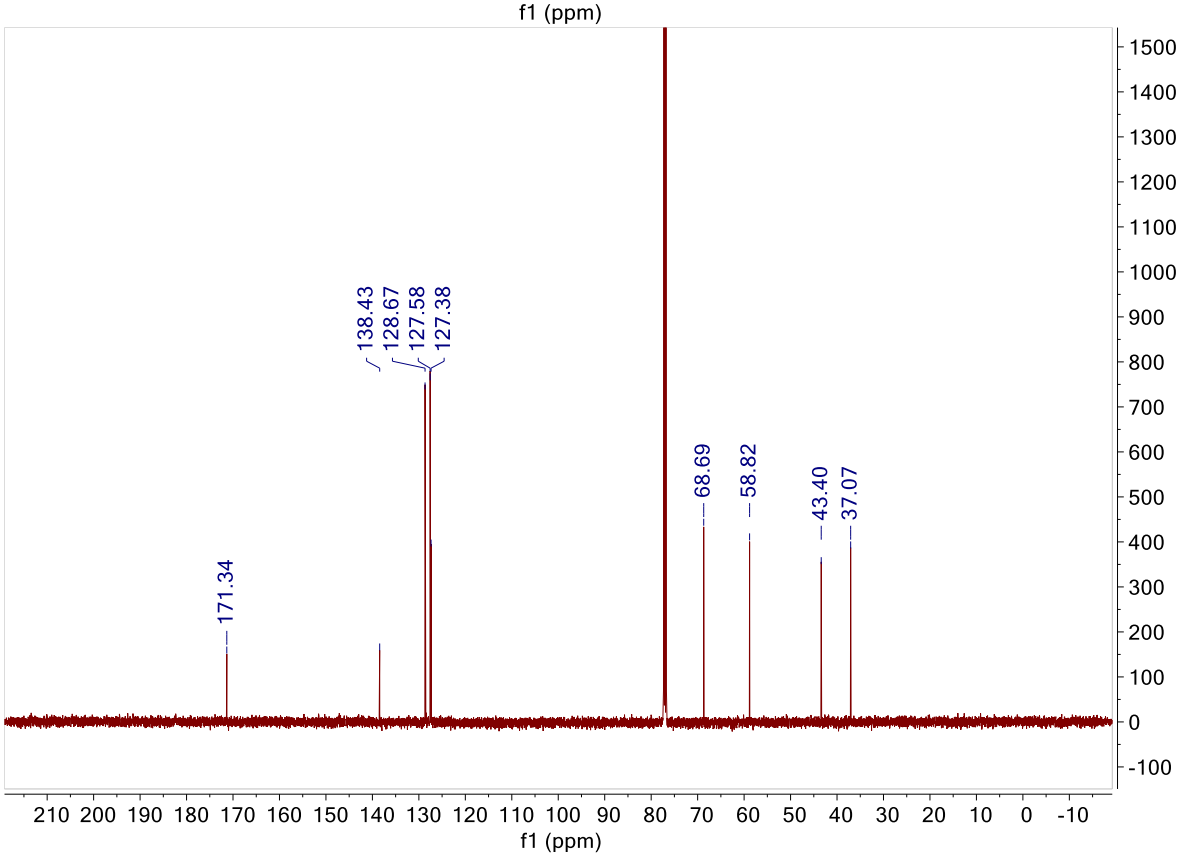
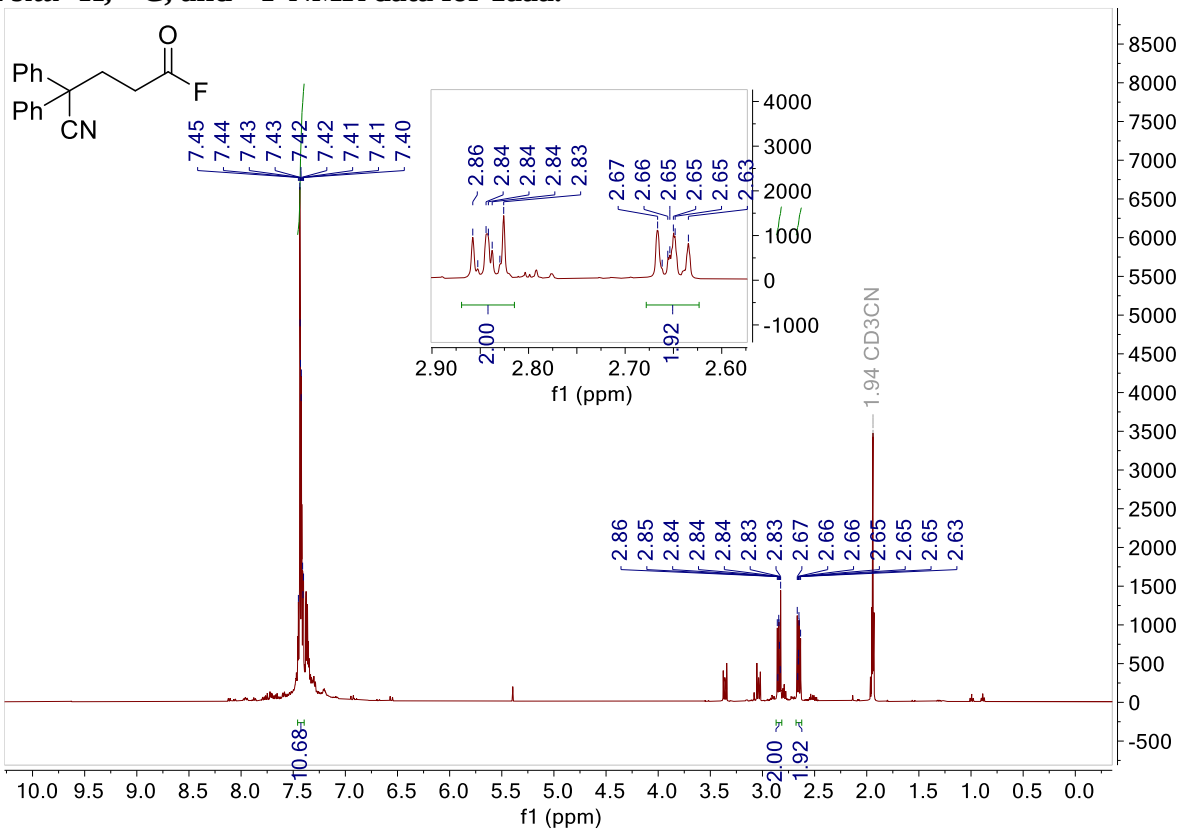
10
-10
-30
-50
-70
-90
-110
f1 (ppm)

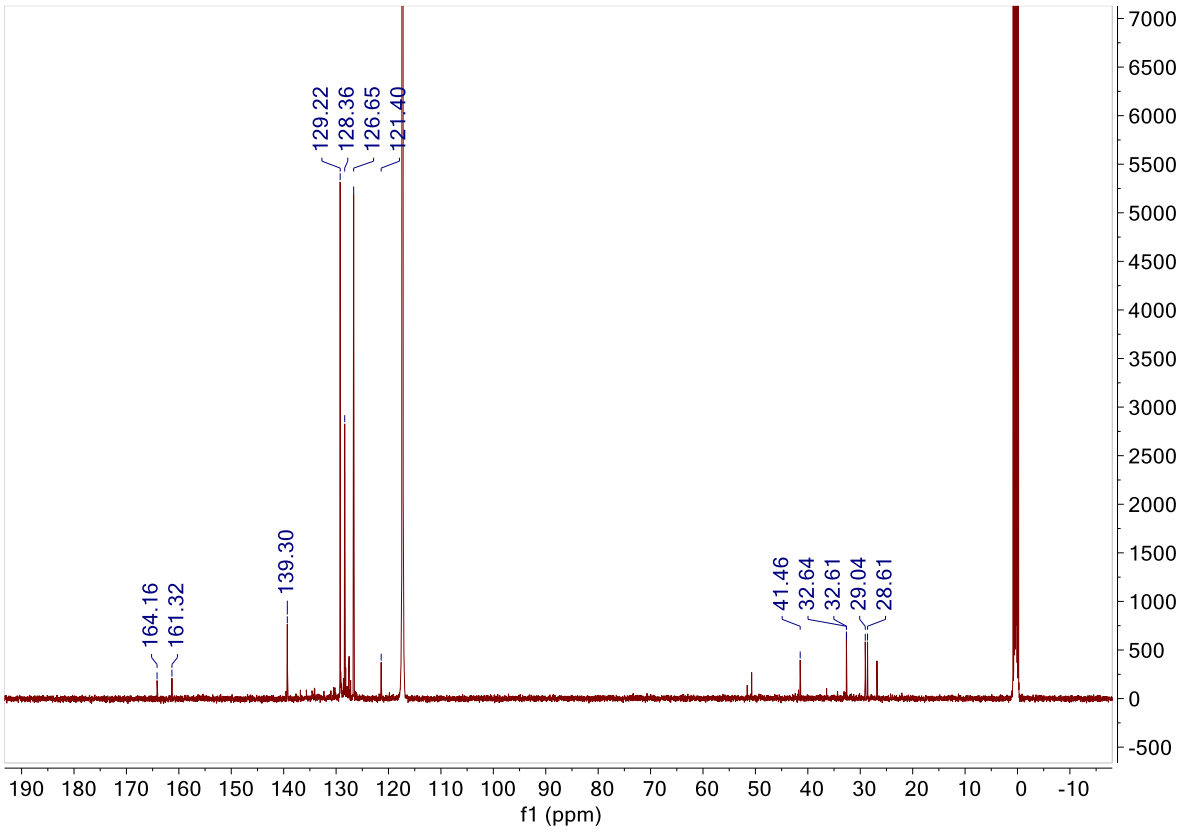
^{1}H and ^{13}C NMR data for 5zz.

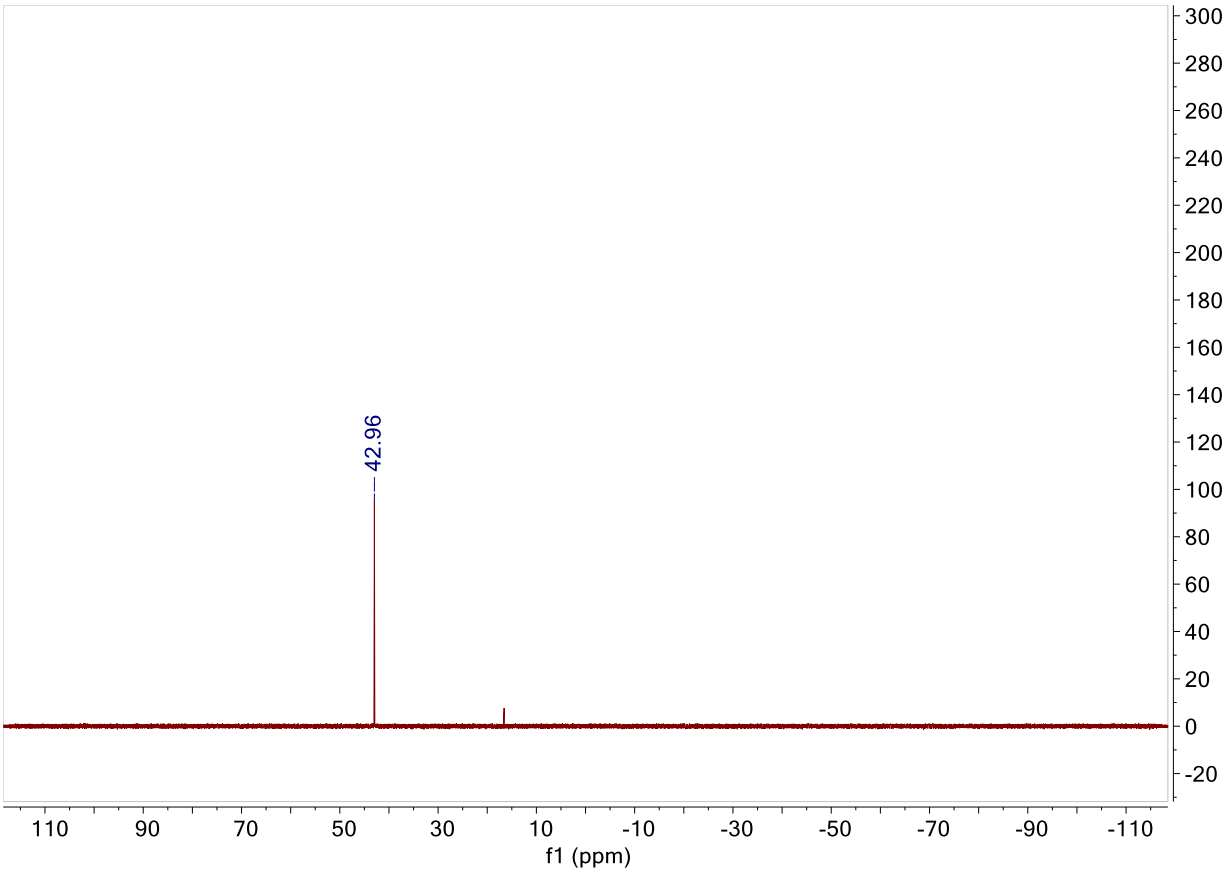




***In situ* ^{1}H, ^{13}C, and ^{19}F NMR data for 1aaa.**






42.96
300
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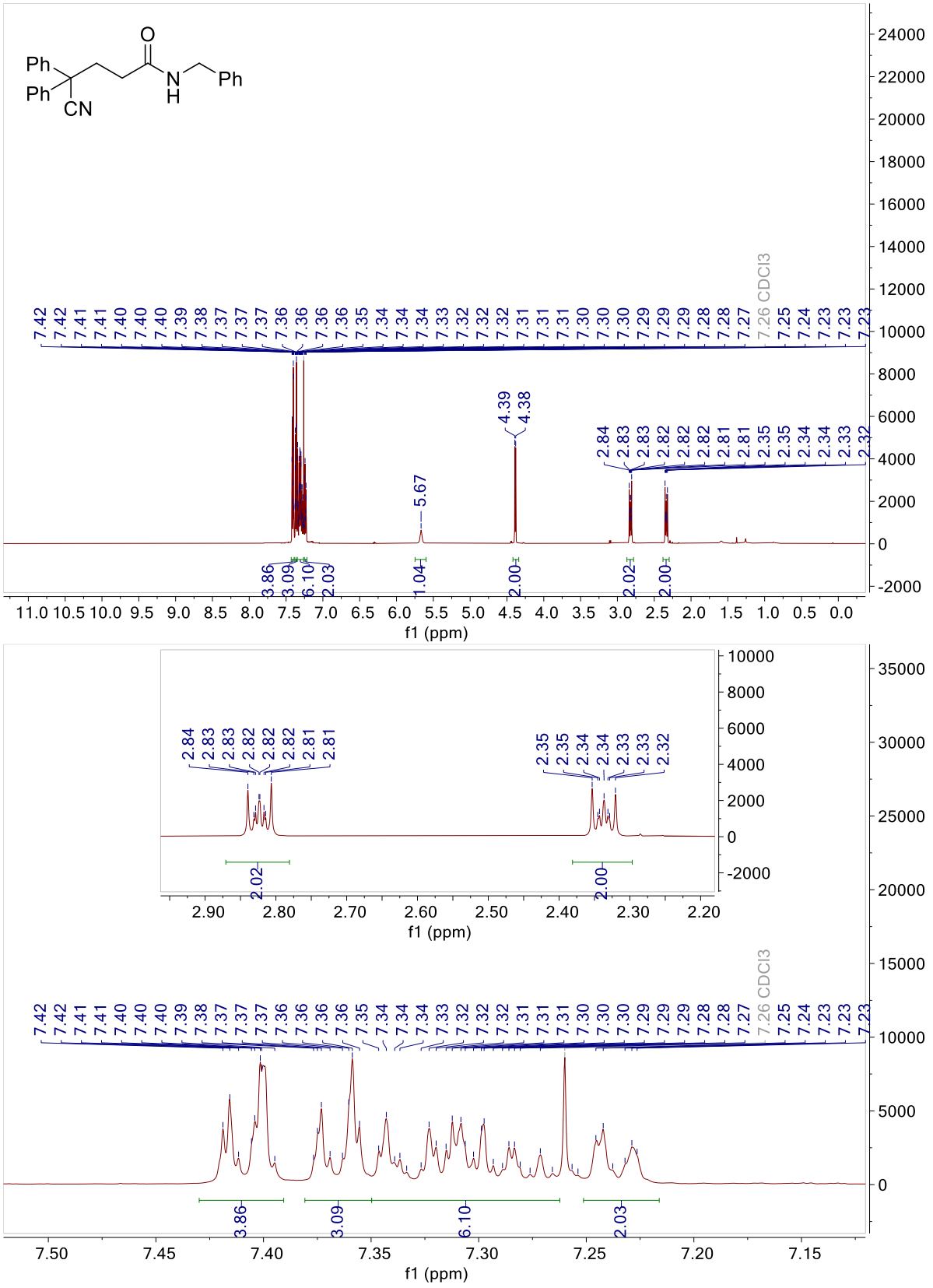
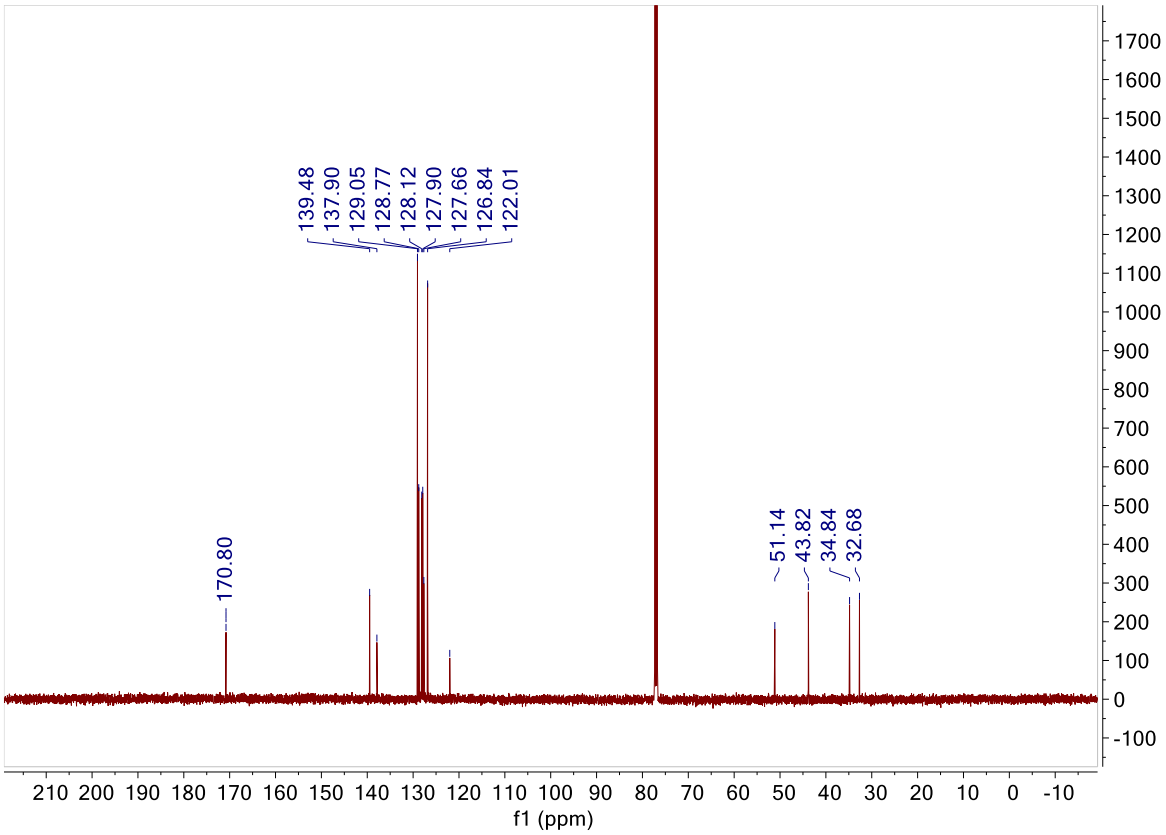
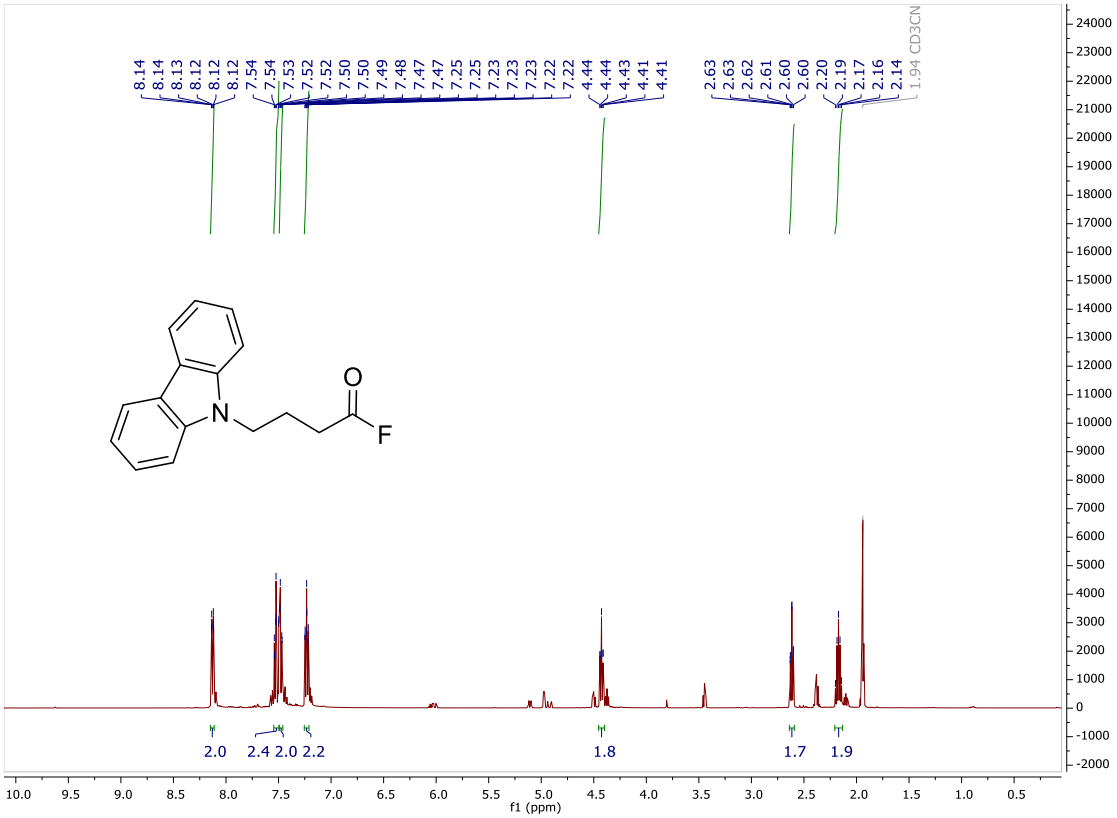
120
100
80
60
40
20
0
-20
110
90
70
50
30
10
-10
-30
-50
-70
-90
-110
f1 (ppm)

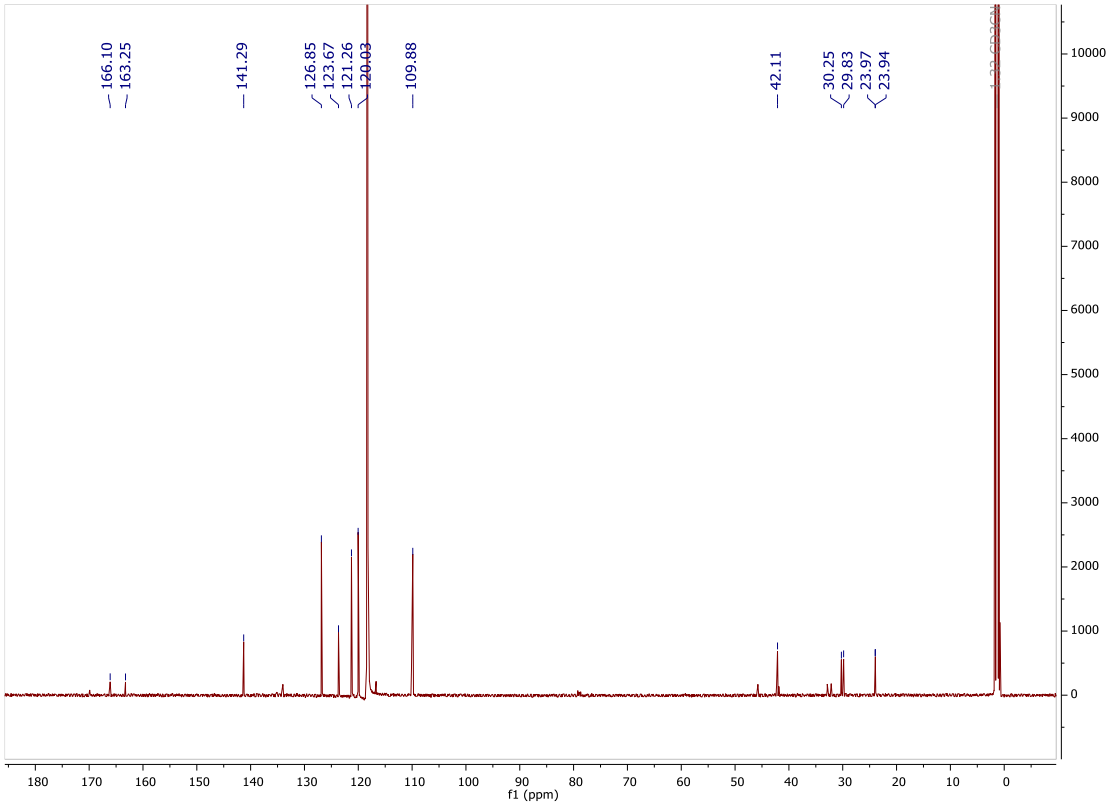
^{1}H and ^{13}C NMR data for 5aaa.

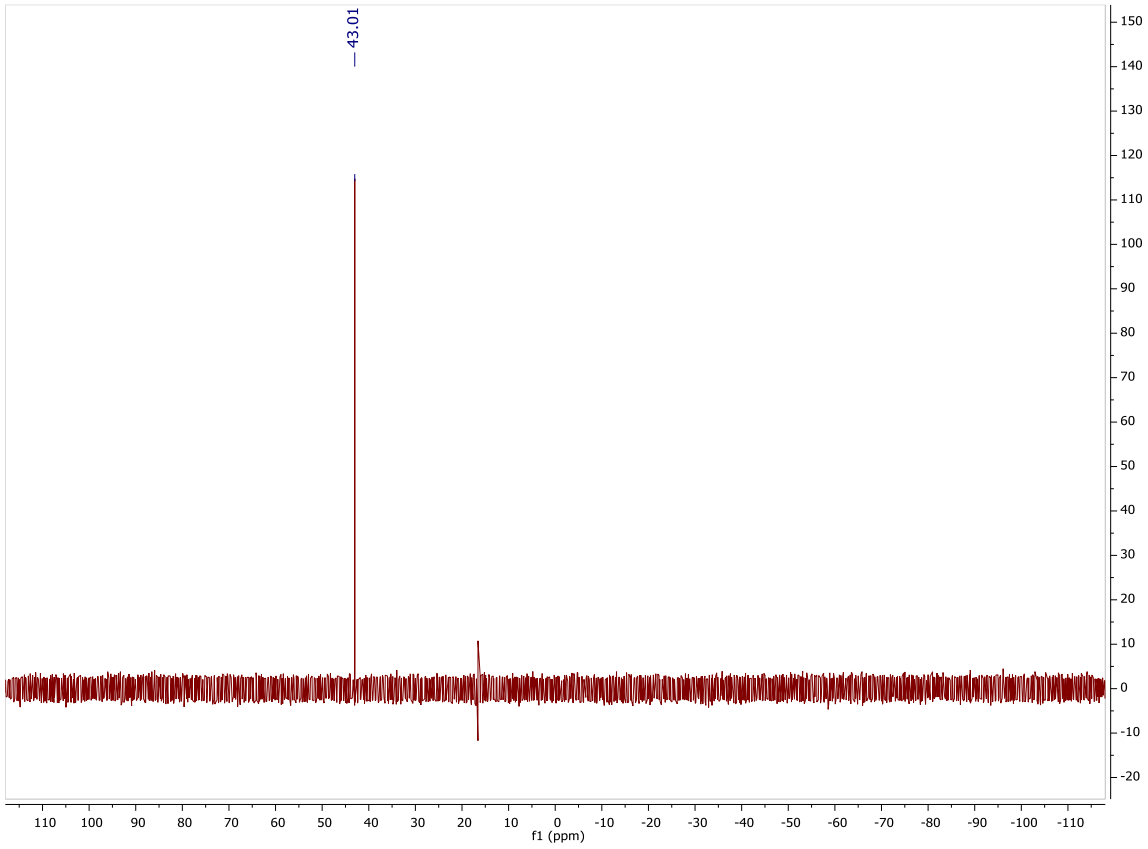



139.48
137.90
129.05
128.77
128.12
127.90
127.66
126.84
122.01
170.80
51.14
43.82
34.84
32.68
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

In situ ^{1}H, ^{13}C, and ^{19}F NMR data for 1bbb






43.01
150
140
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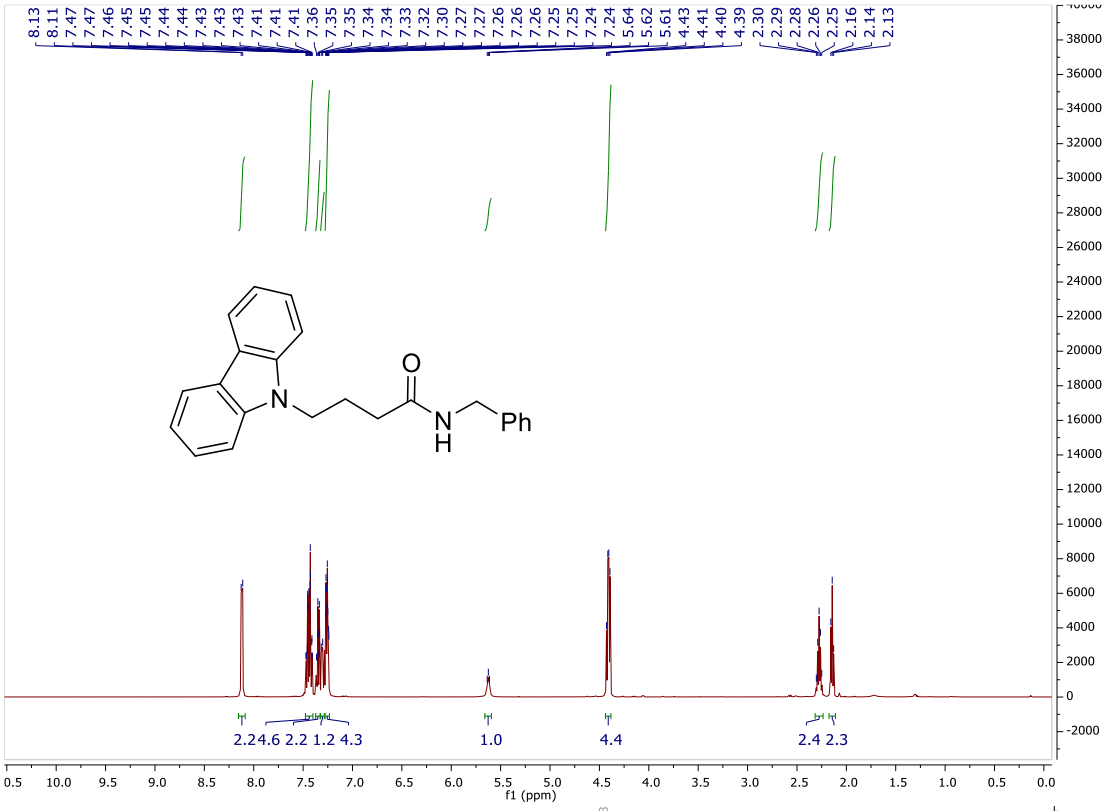
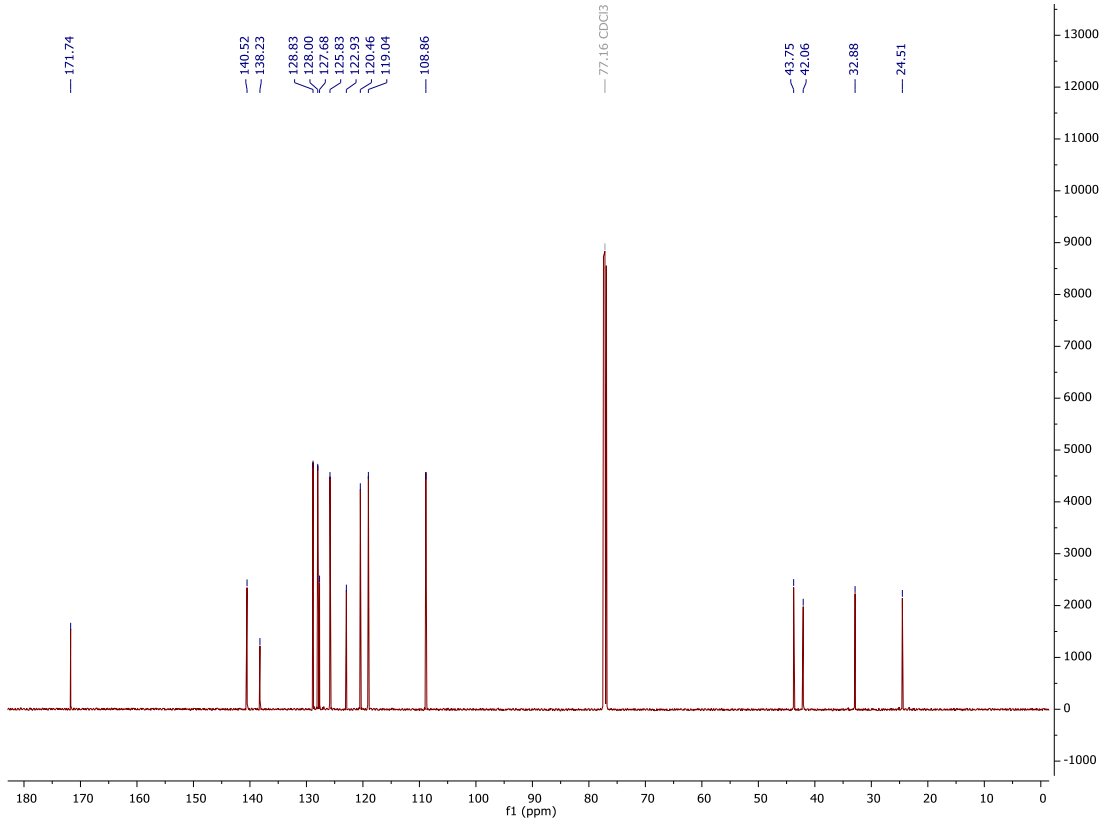
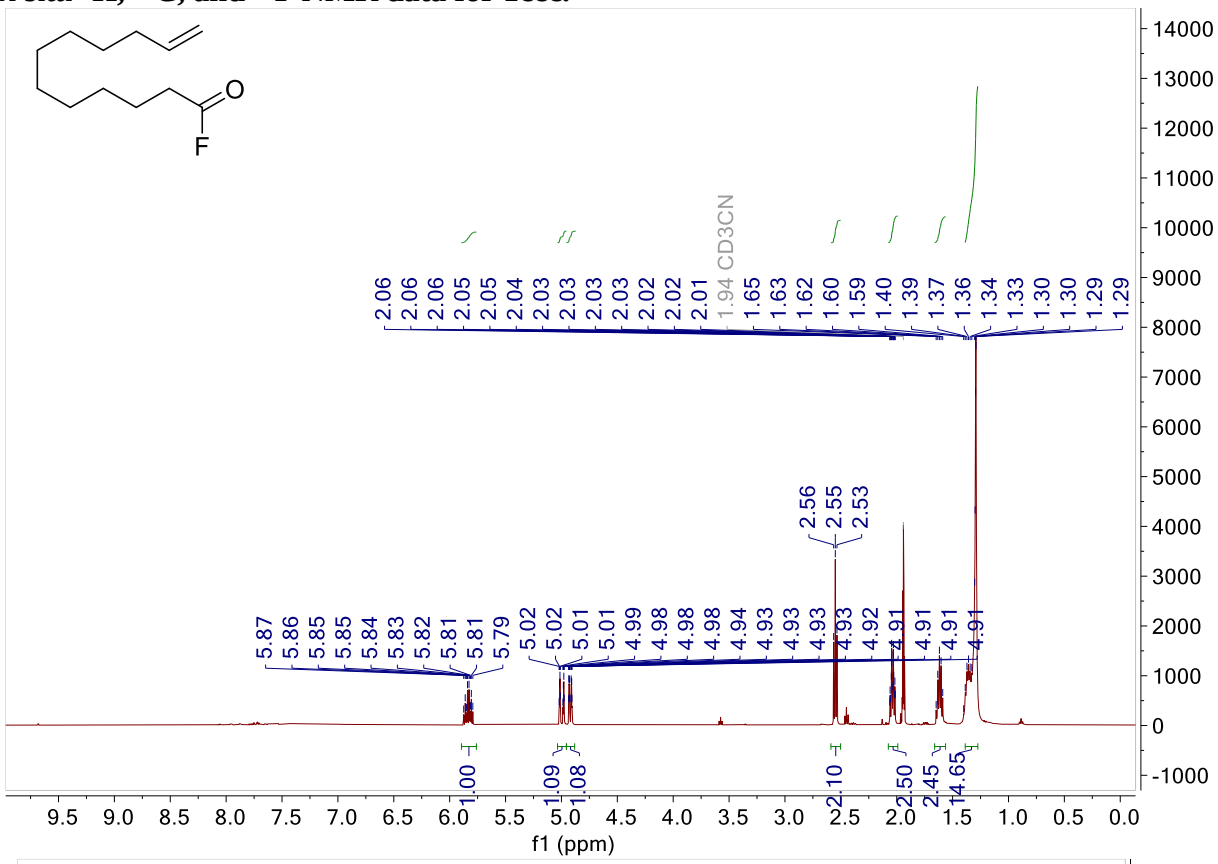
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110
f1 (ppm)

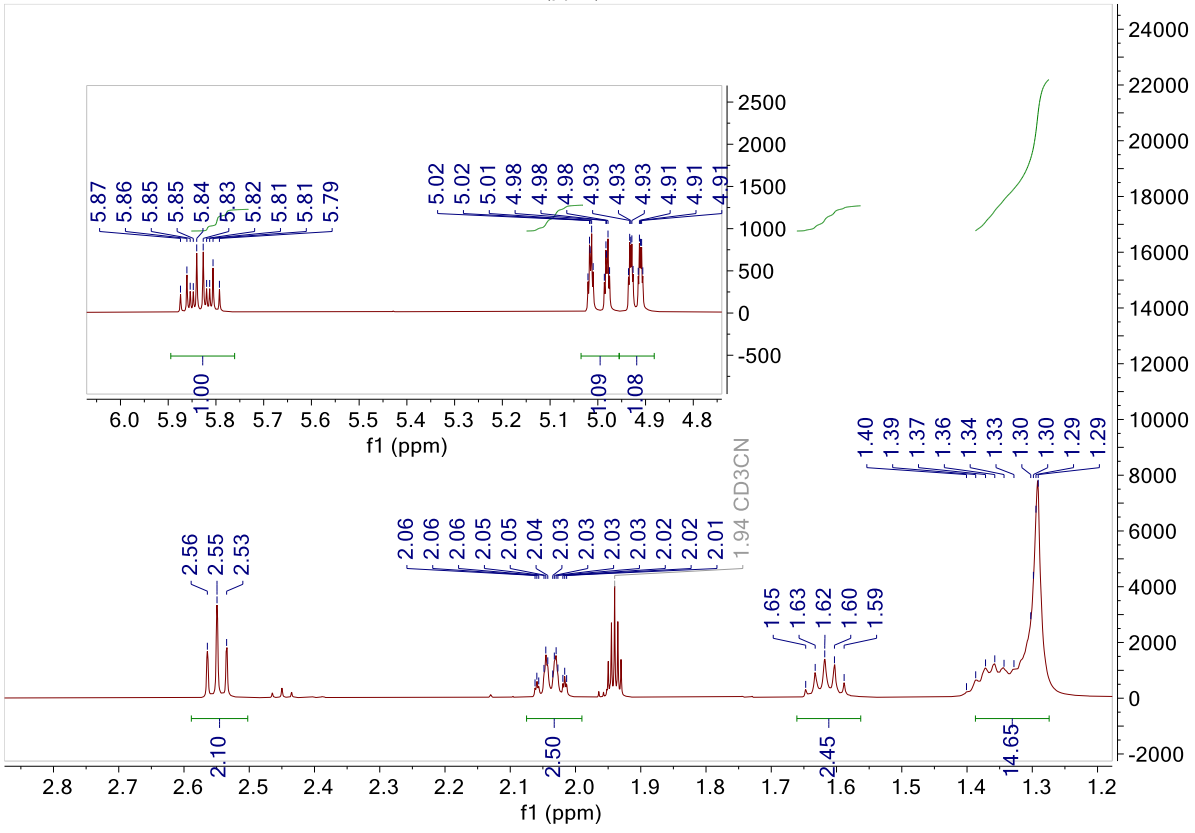
^{1}H and ^{13}C NMR data for 4bbb

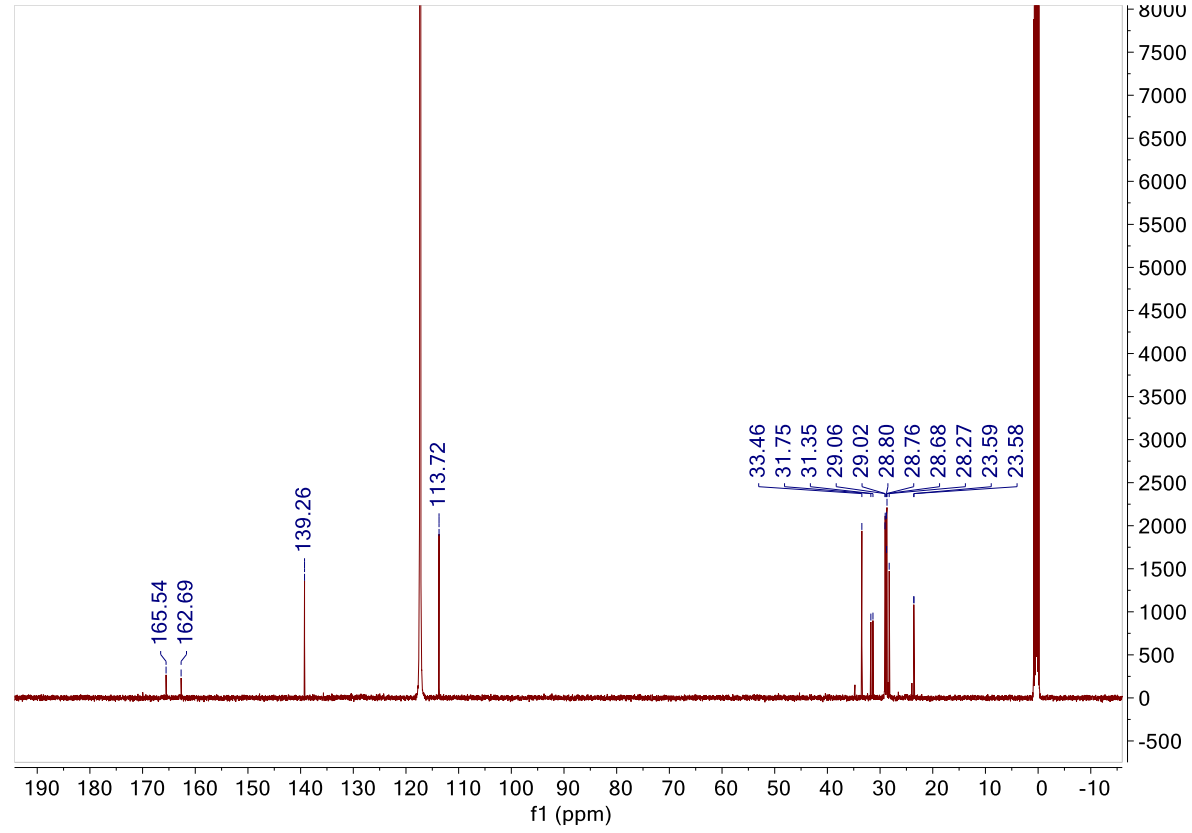


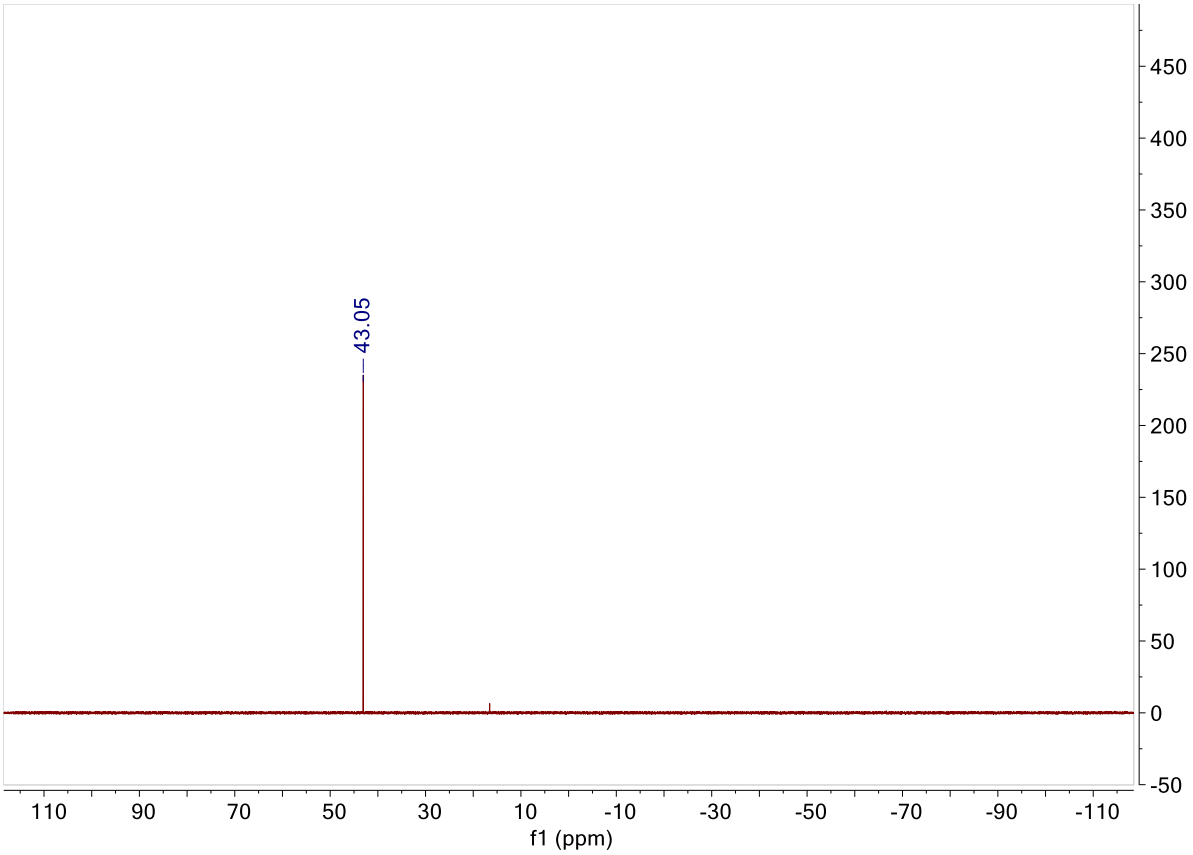


***In situ* ^{1}H, ^{13}C, and ^{19}F NMR data for 1ccc.**

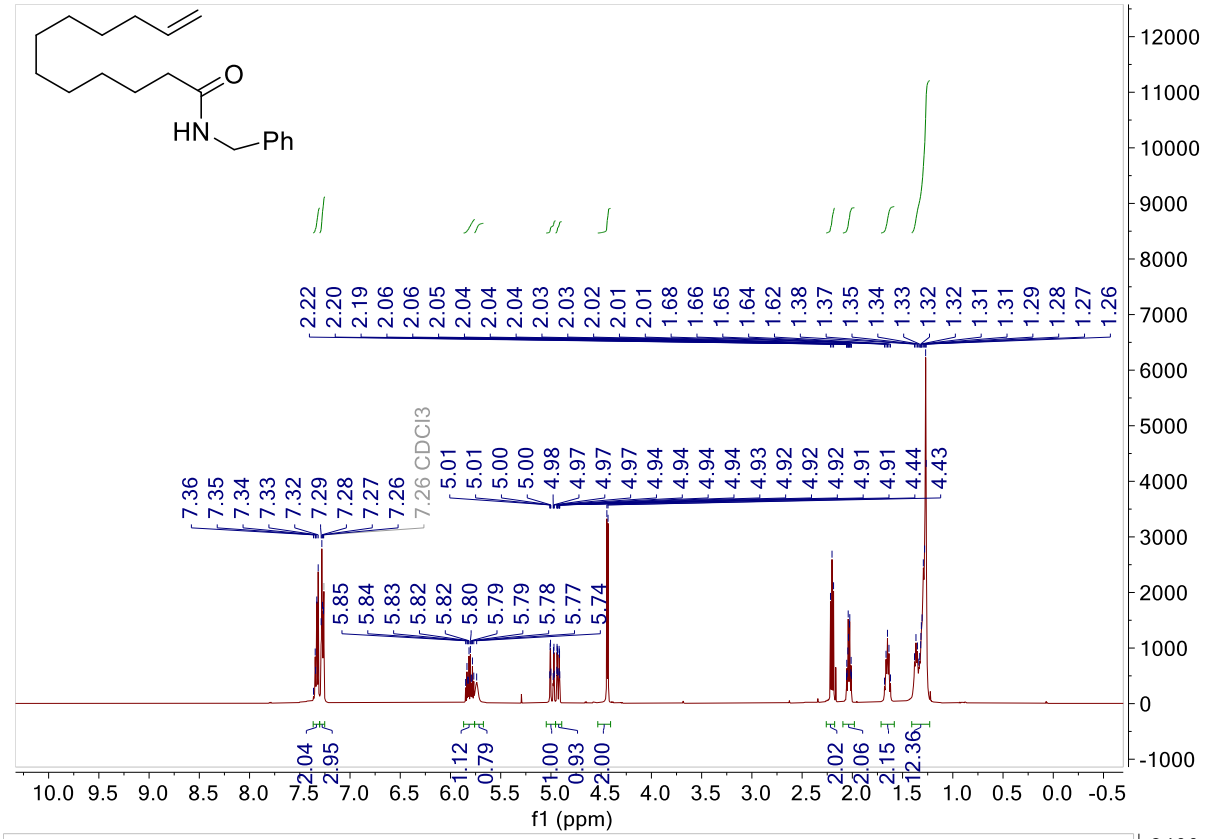


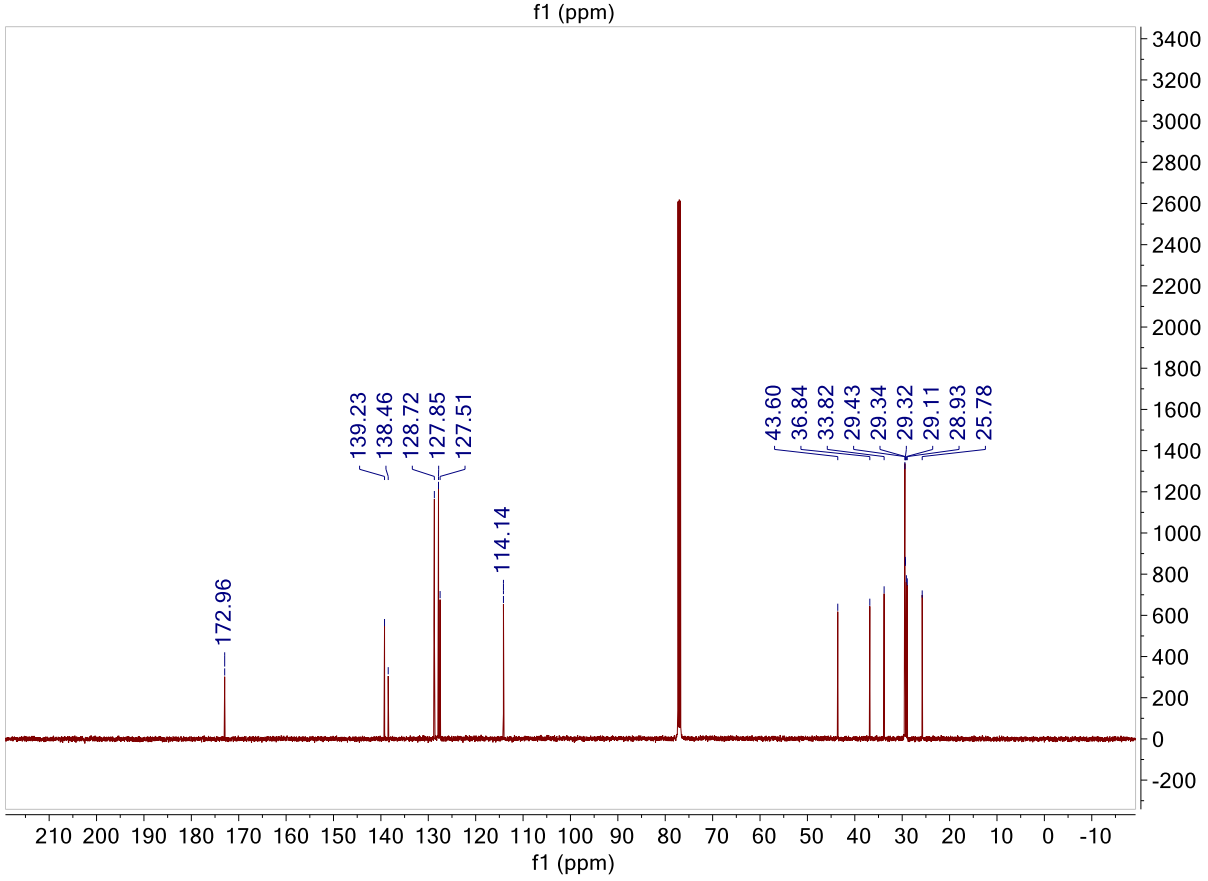



165.54
162.69
139.26
113.72
33.46
31.75
31.35
29.06
29.02
28.80
28.76
28.68
28.27
23.59
23.58
f1 (ppm)

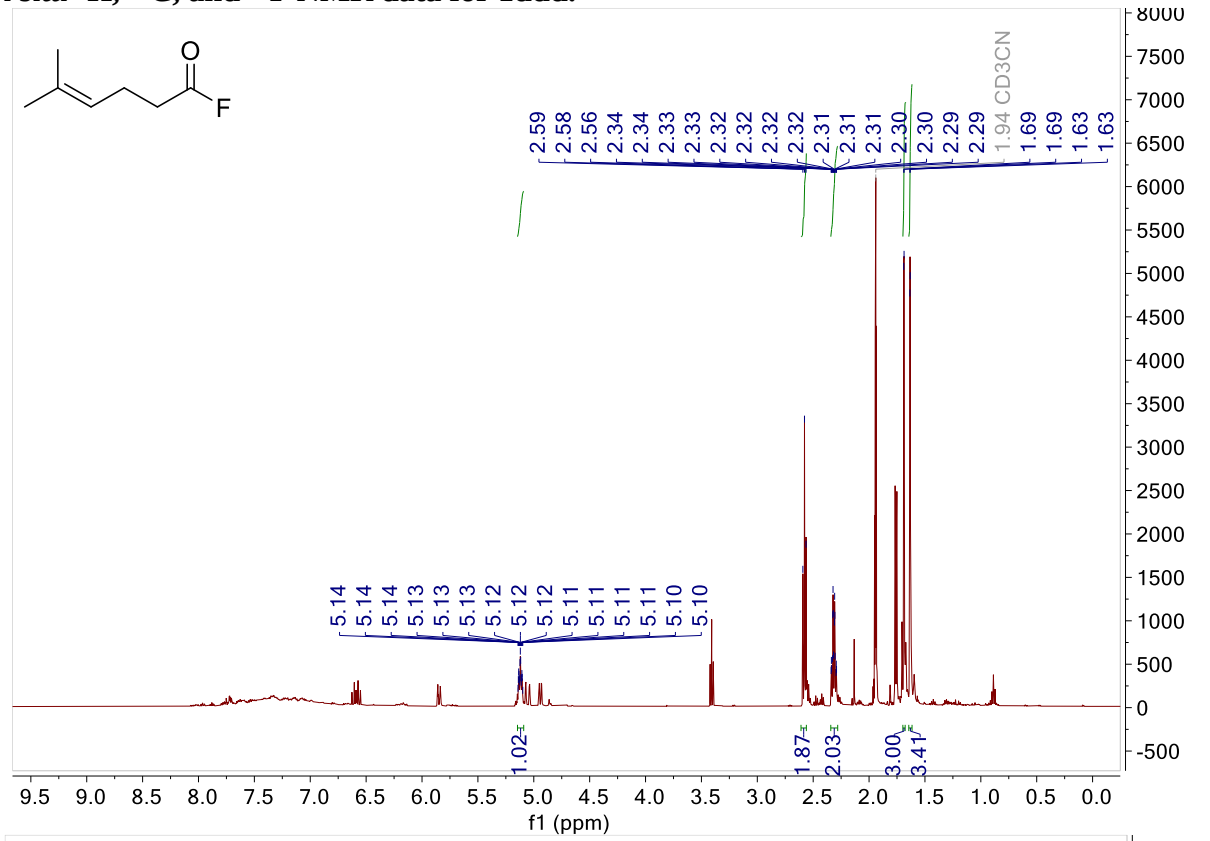

43.05
f1 (ppm)

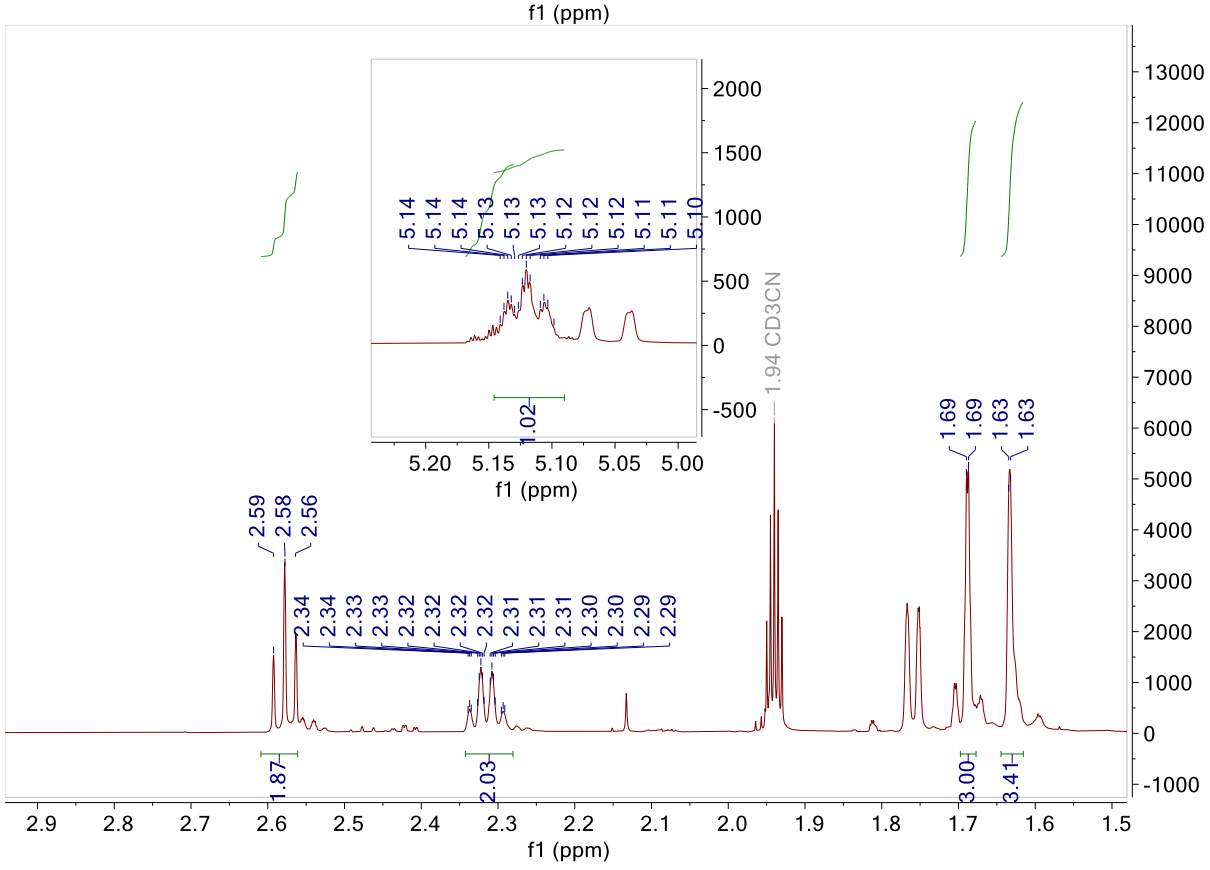
^{1}H and ^{13}C NMR data for 5ccc.

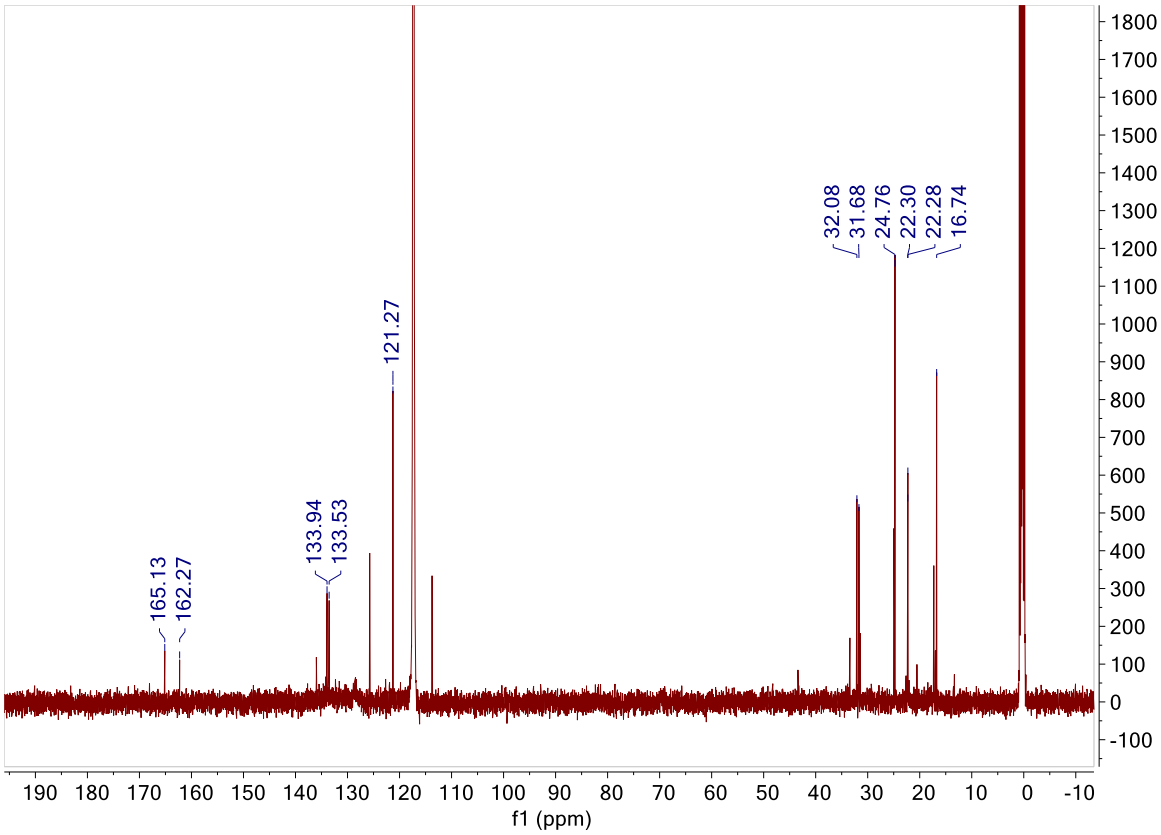




***In situ* ^{1}H, ^{13}C, and ^{19}F NMR data for 1ddd.**






32.08
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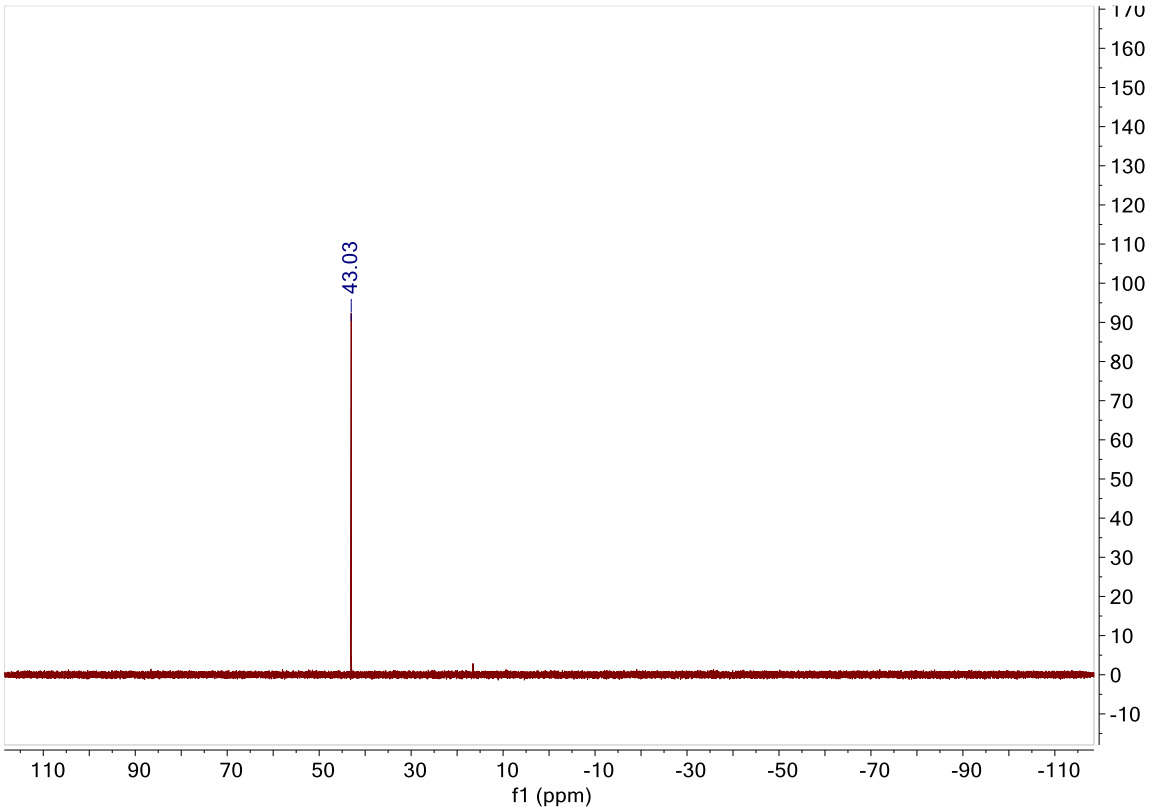
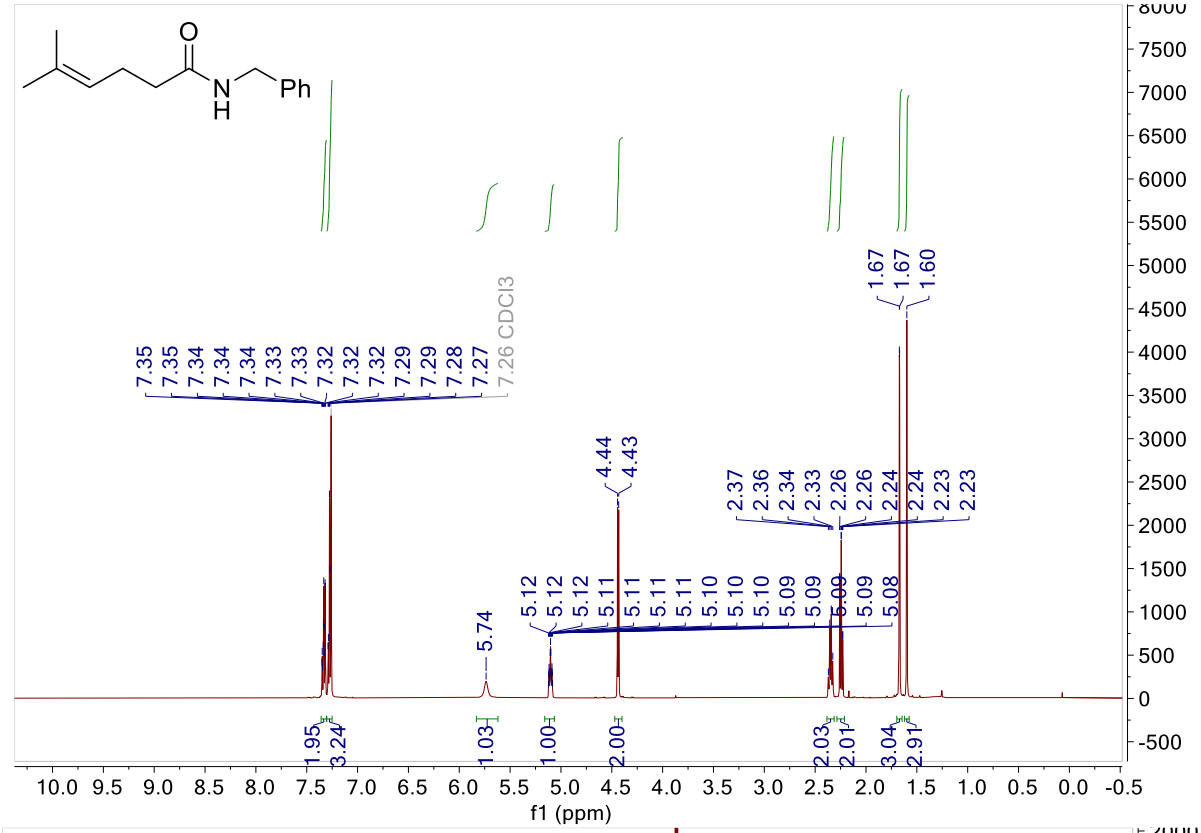
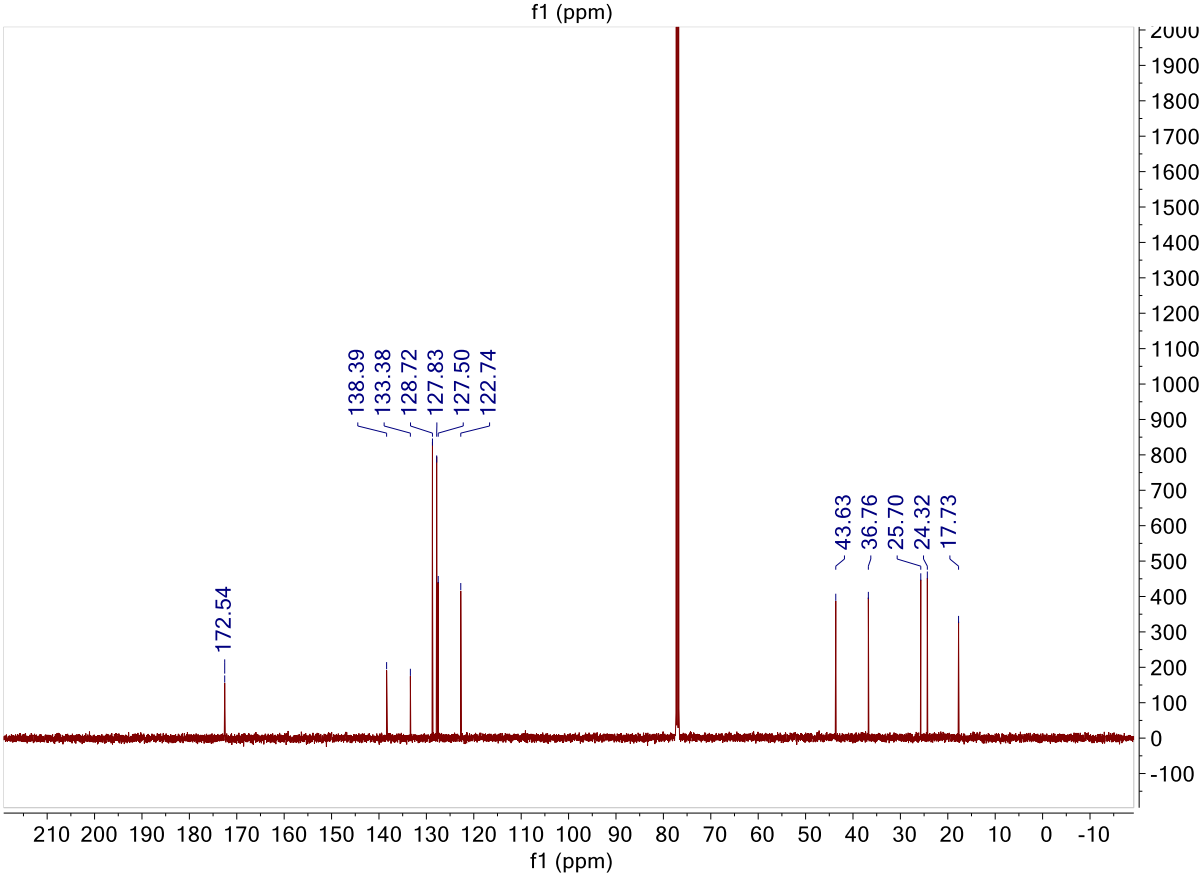
22.30
22.28
16.74
121.27
133.94
133.53
165.13
162.27
f1 (ppm)

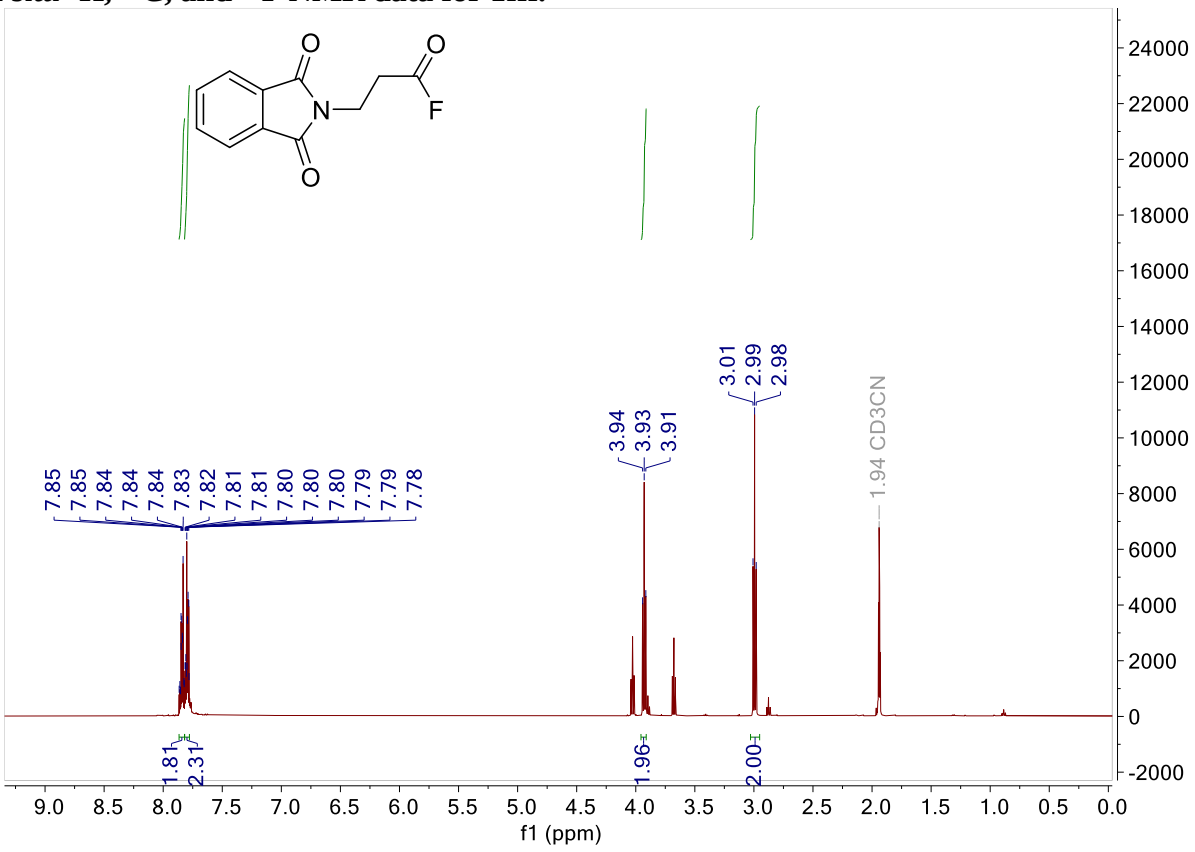

43.03
f1 (ppm)

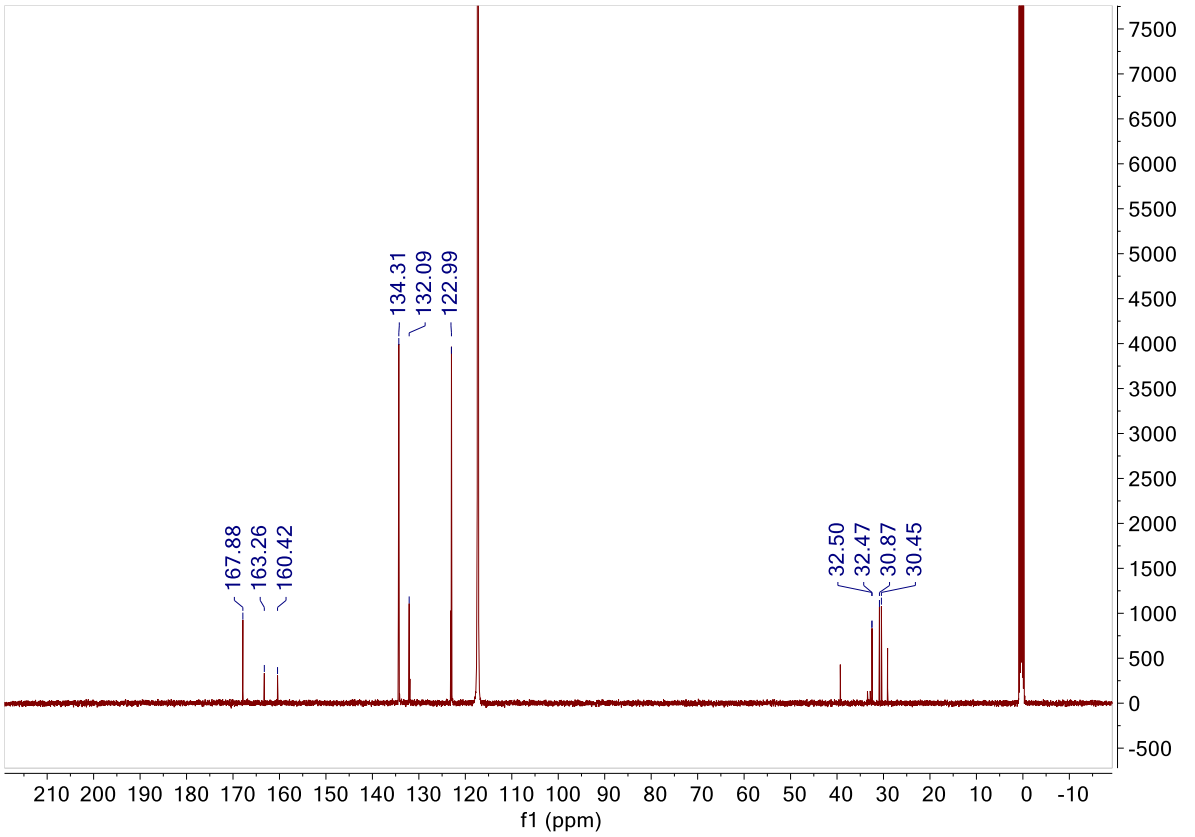
^{1}H and ^{13}C NMR data for 5ddd.

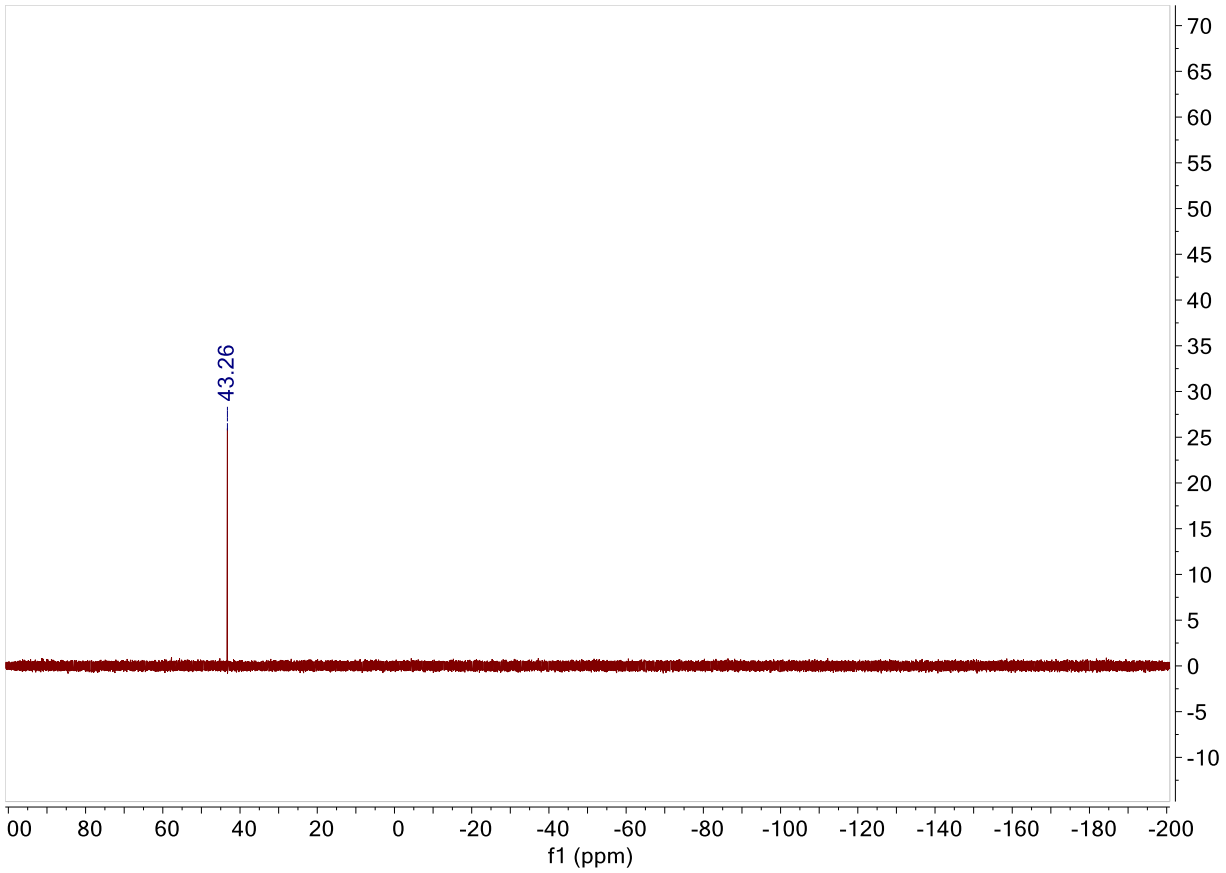




***In situ* ^{1}H, ^{13}C, and ^{19}F NMR data for 1fff.**






43.26
70
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60
55
50
45
40
35
30
25
20
15
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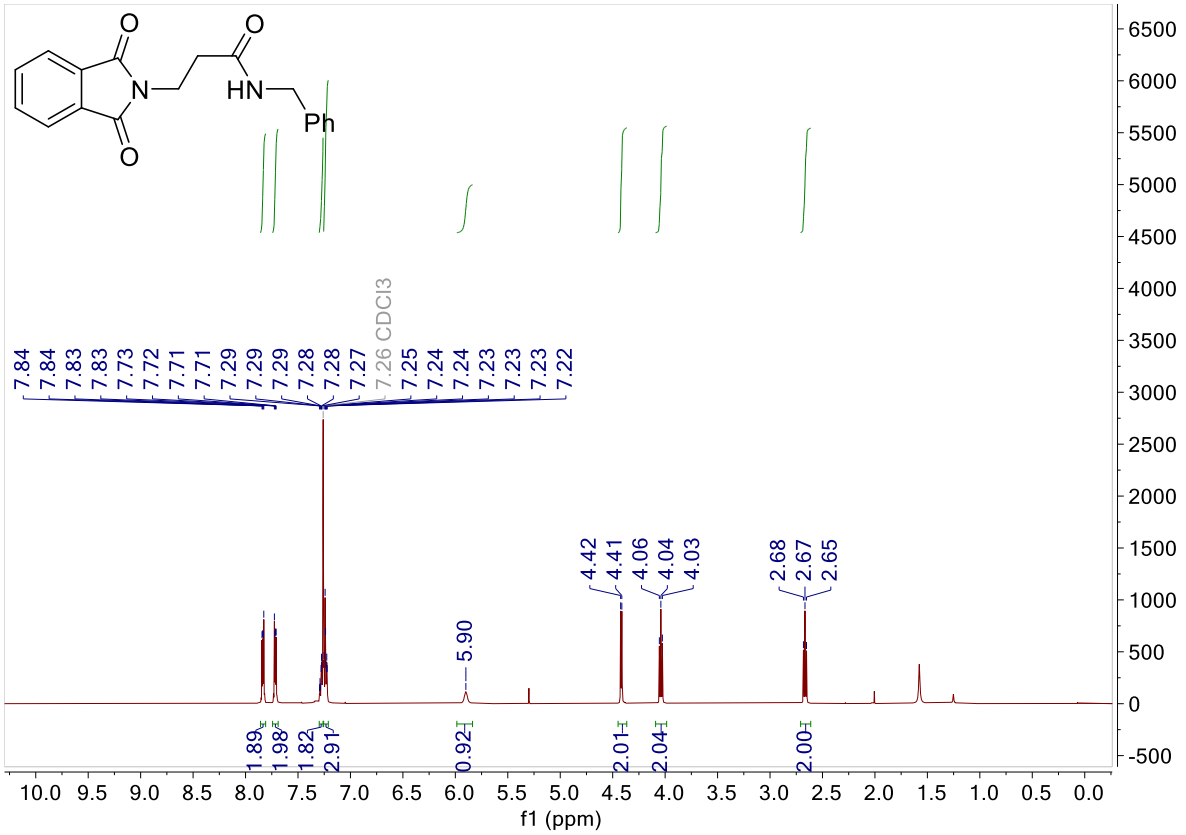
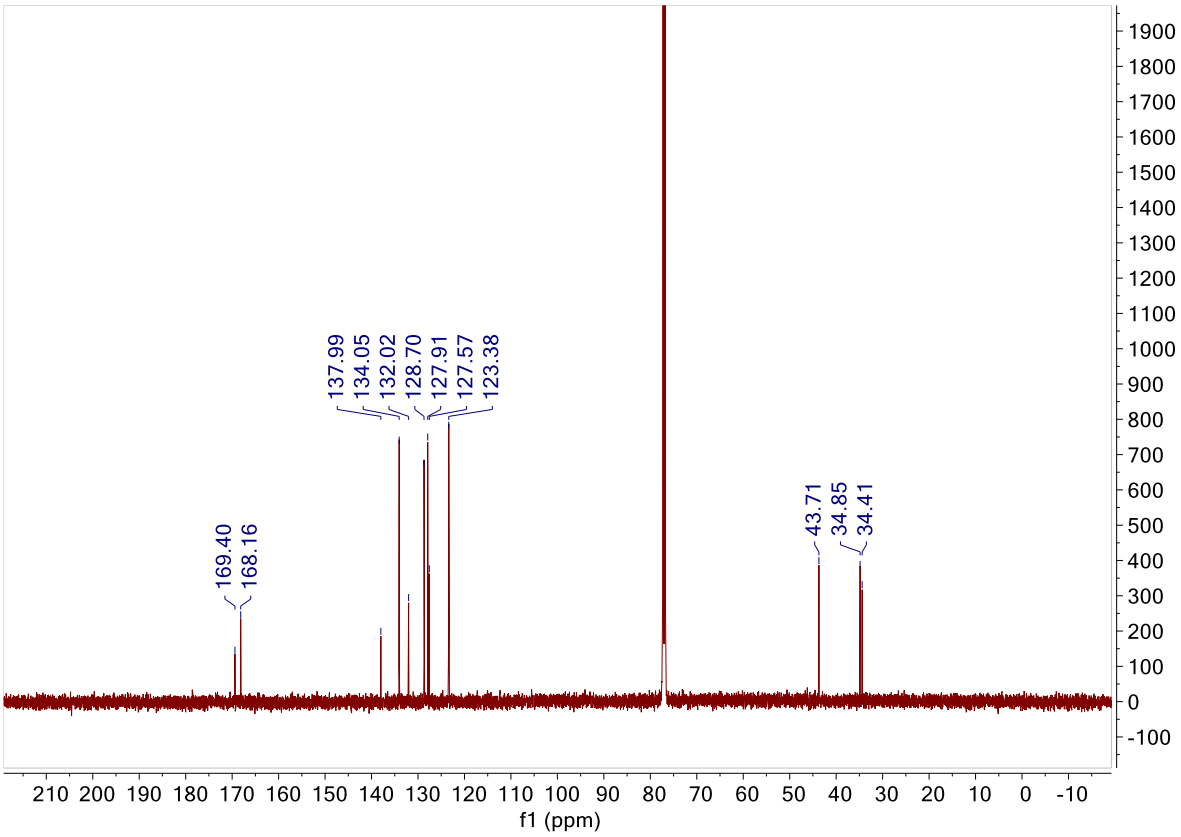
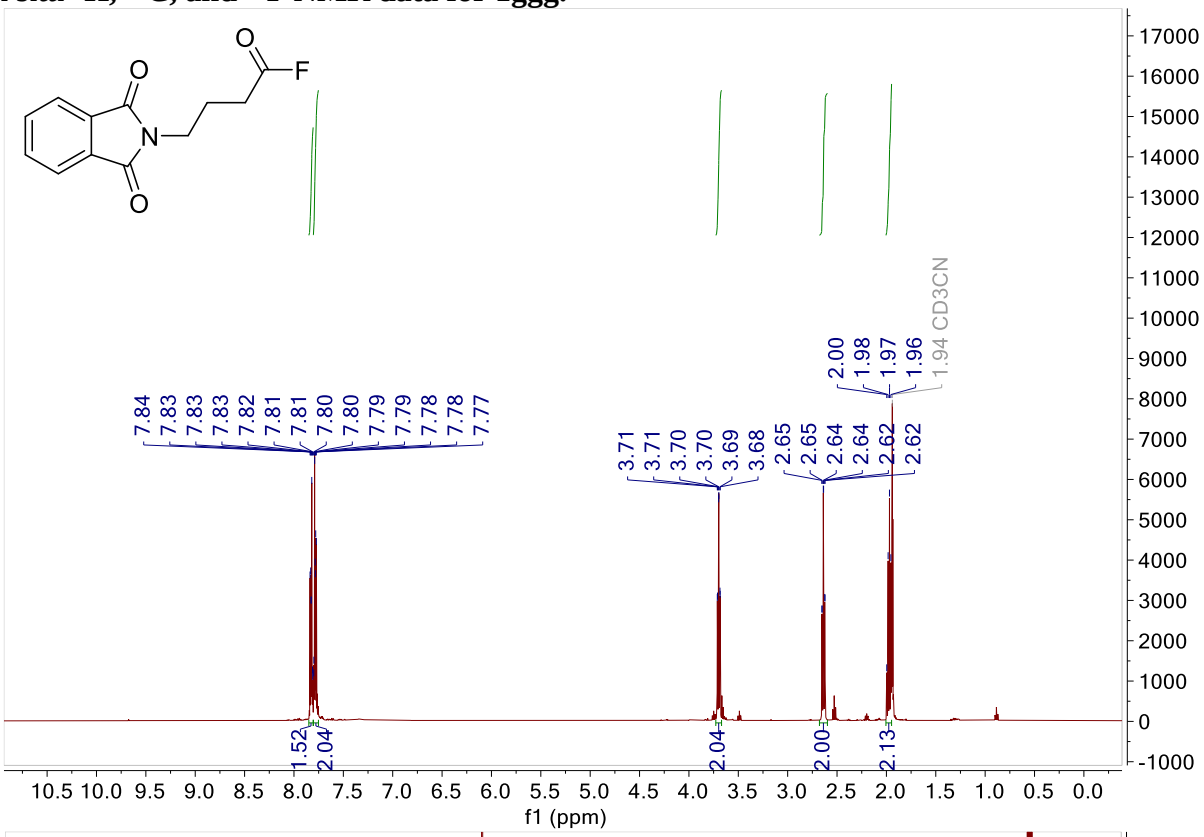
5
0
-5
-10
00
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

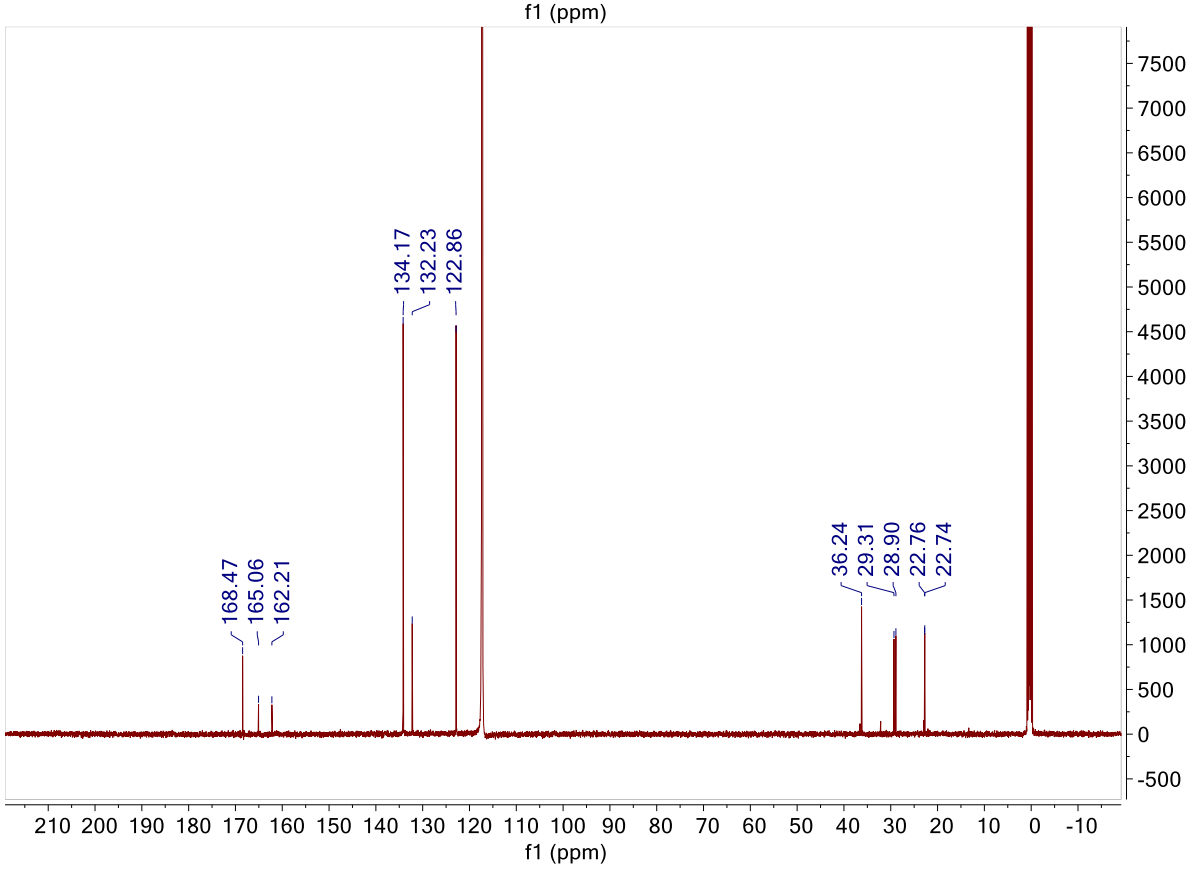
^{1}H and ^{13}C NMR data for 5fff.

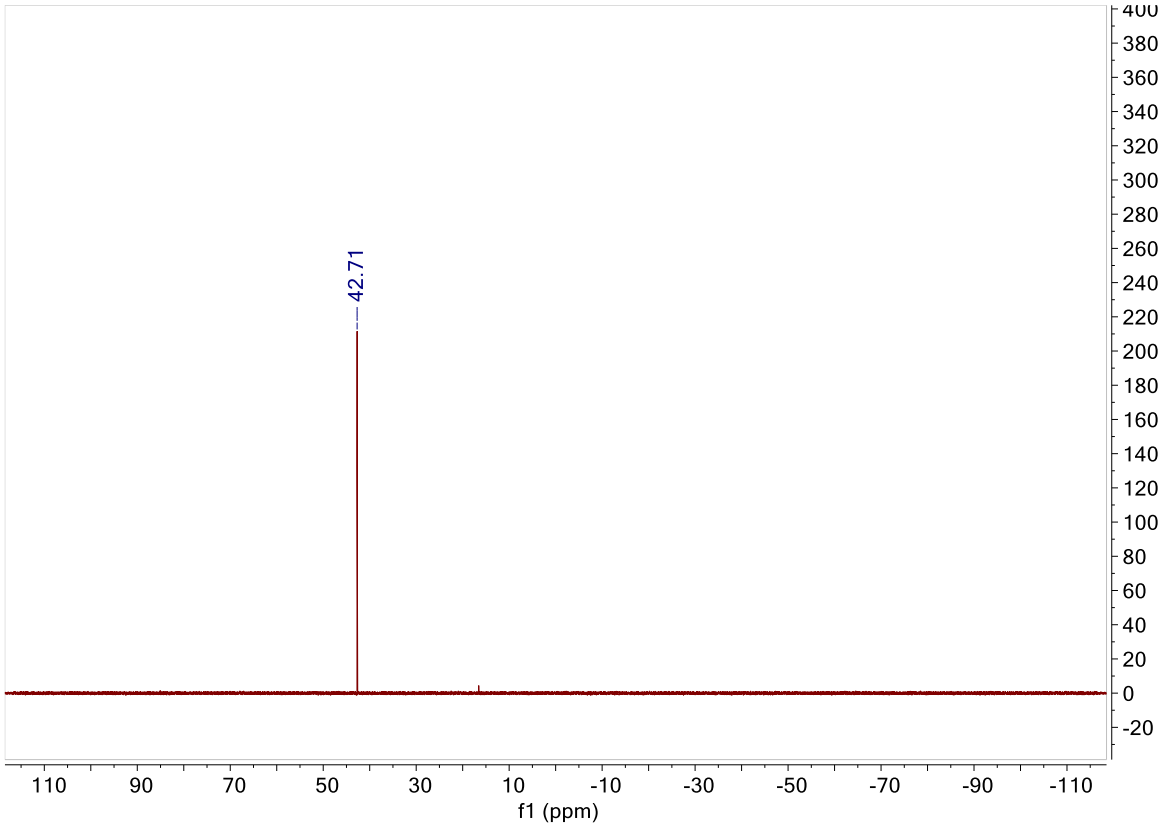




***In situ* ^{1}H, ^{13}C, and ^{19}F NMR data for 1ggg.**






42.71
400
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340
320
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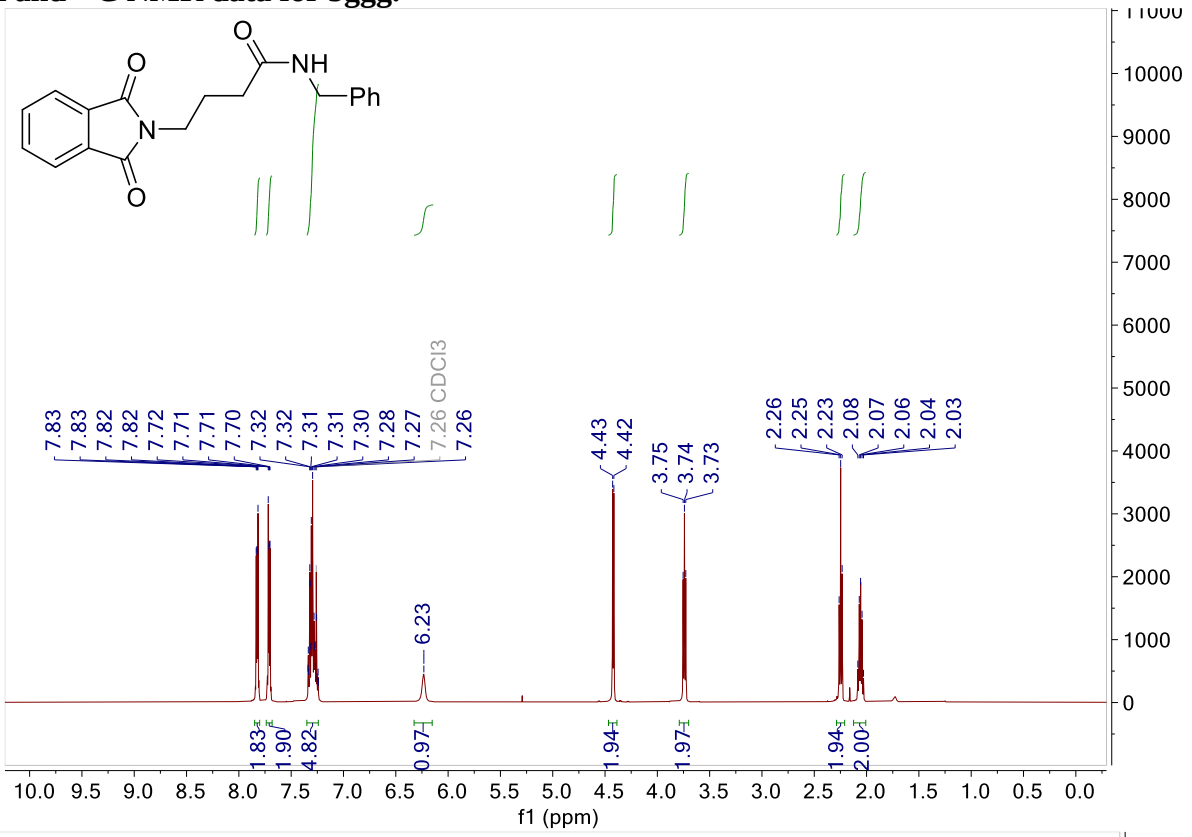
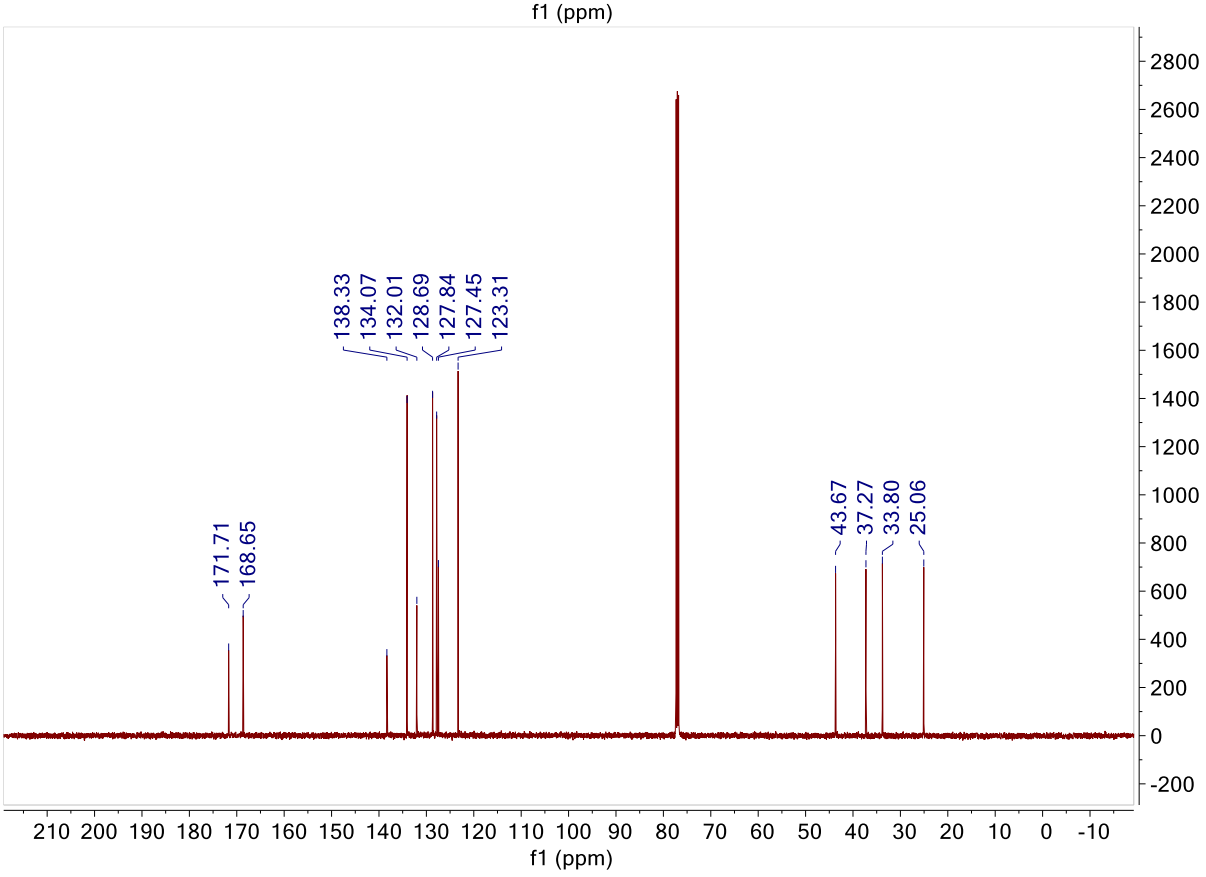
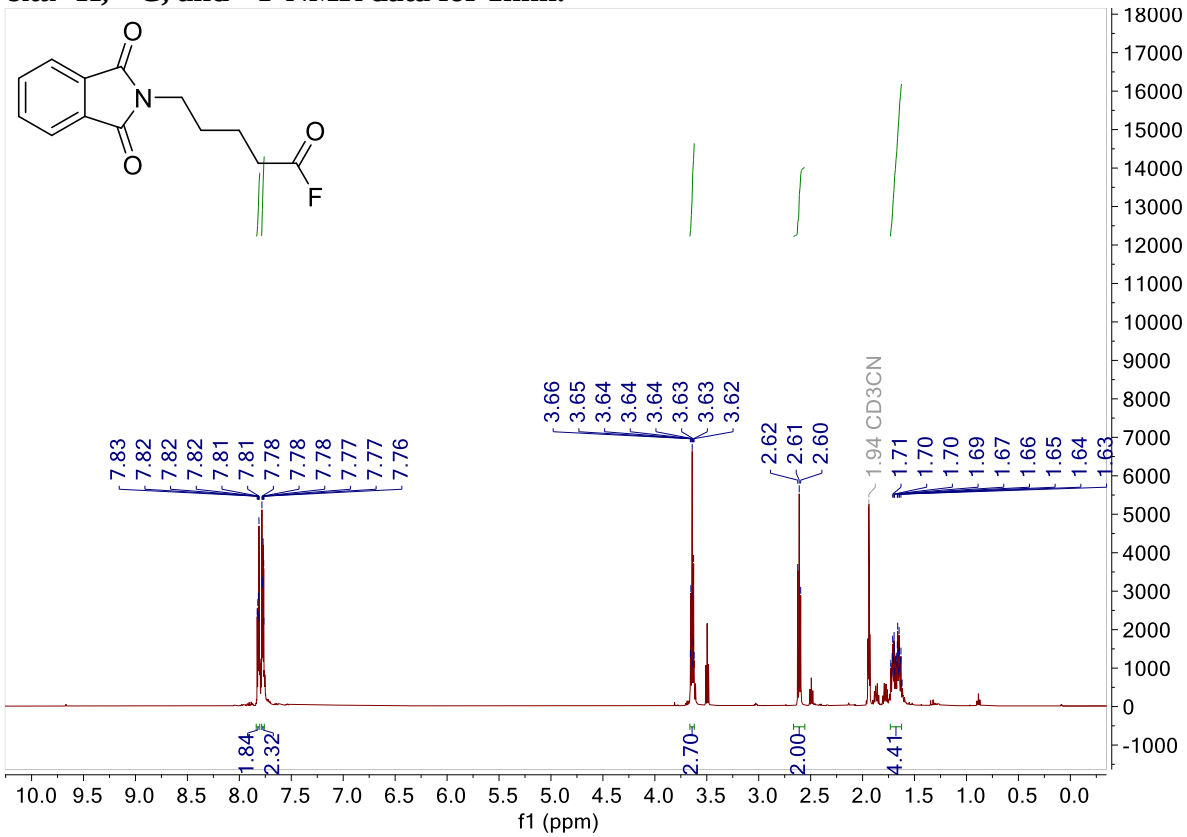
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
110
90
70
50
30
10
-10
-30
-50
-70
-90
-110
f1 (ppm)

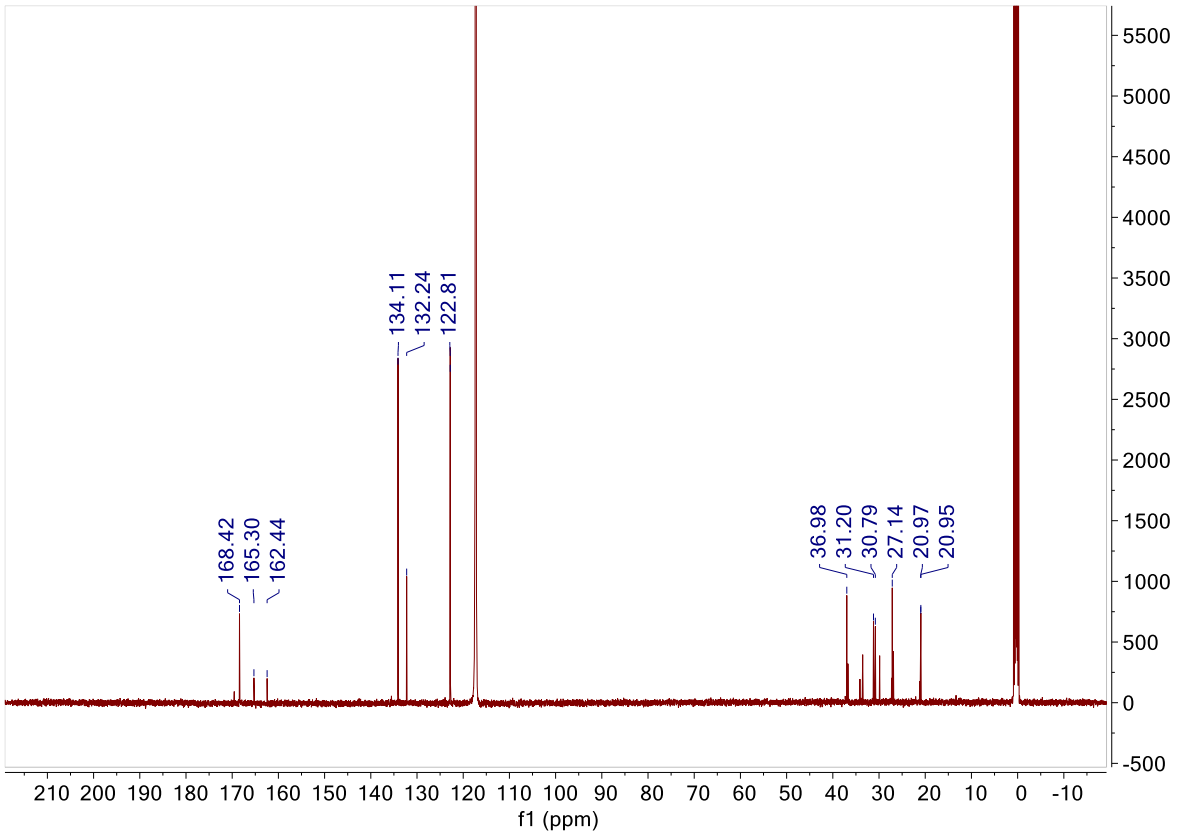
^{1}H and ^{13}C NMR data for 5ggg.

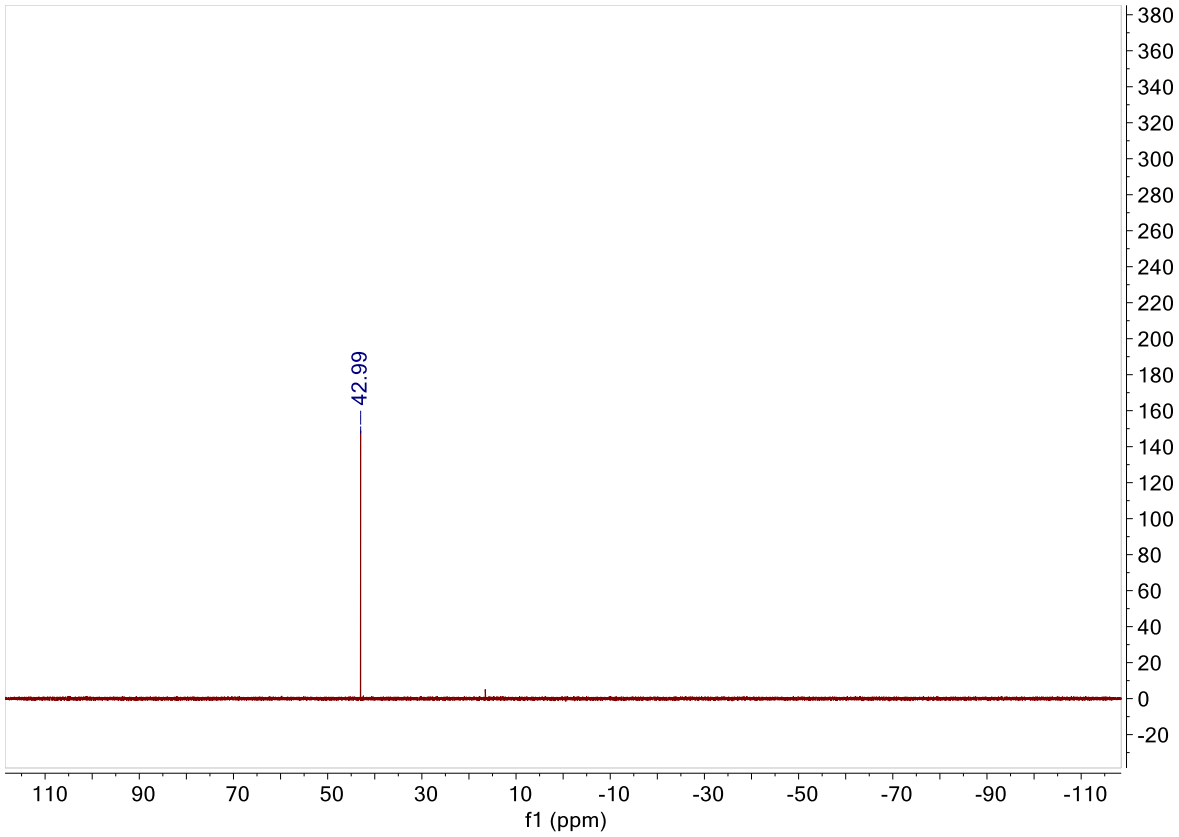




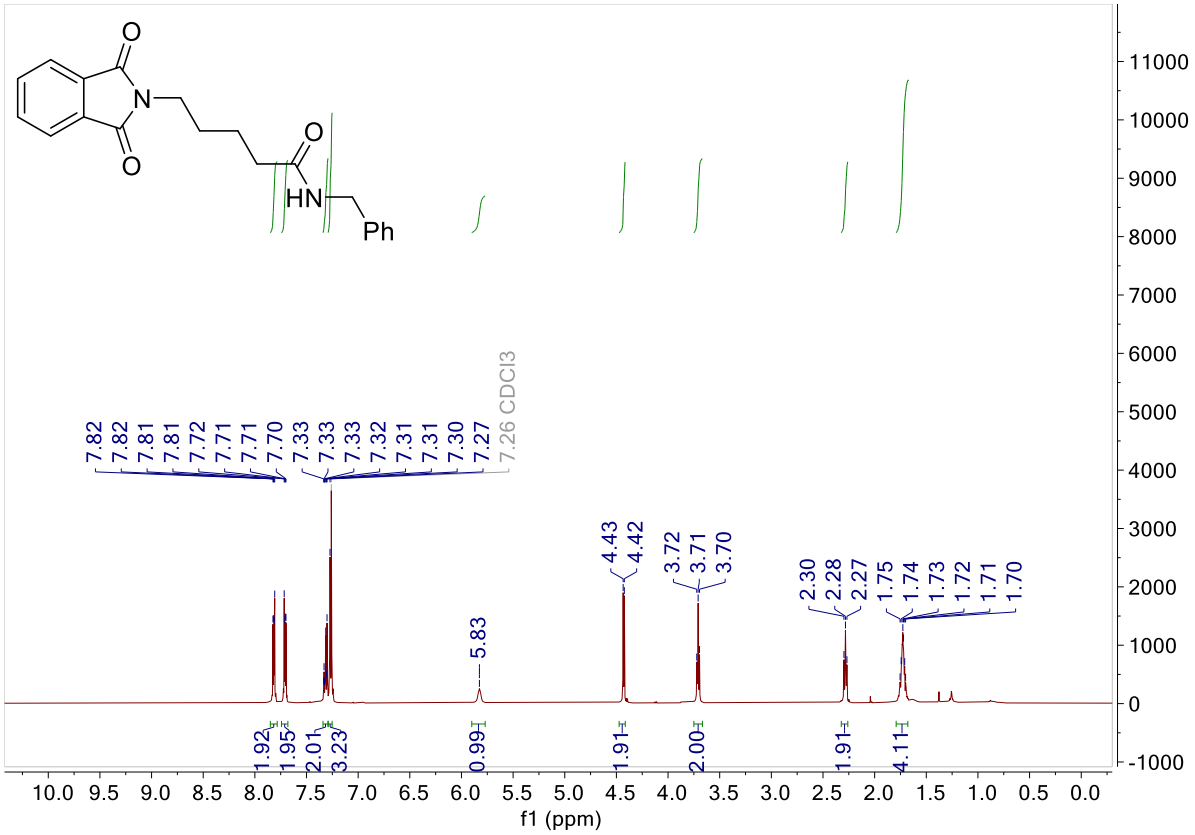
***In situ* ^{1}H, ^{13}C, and ^{19}F NMR data for 1hhh.**

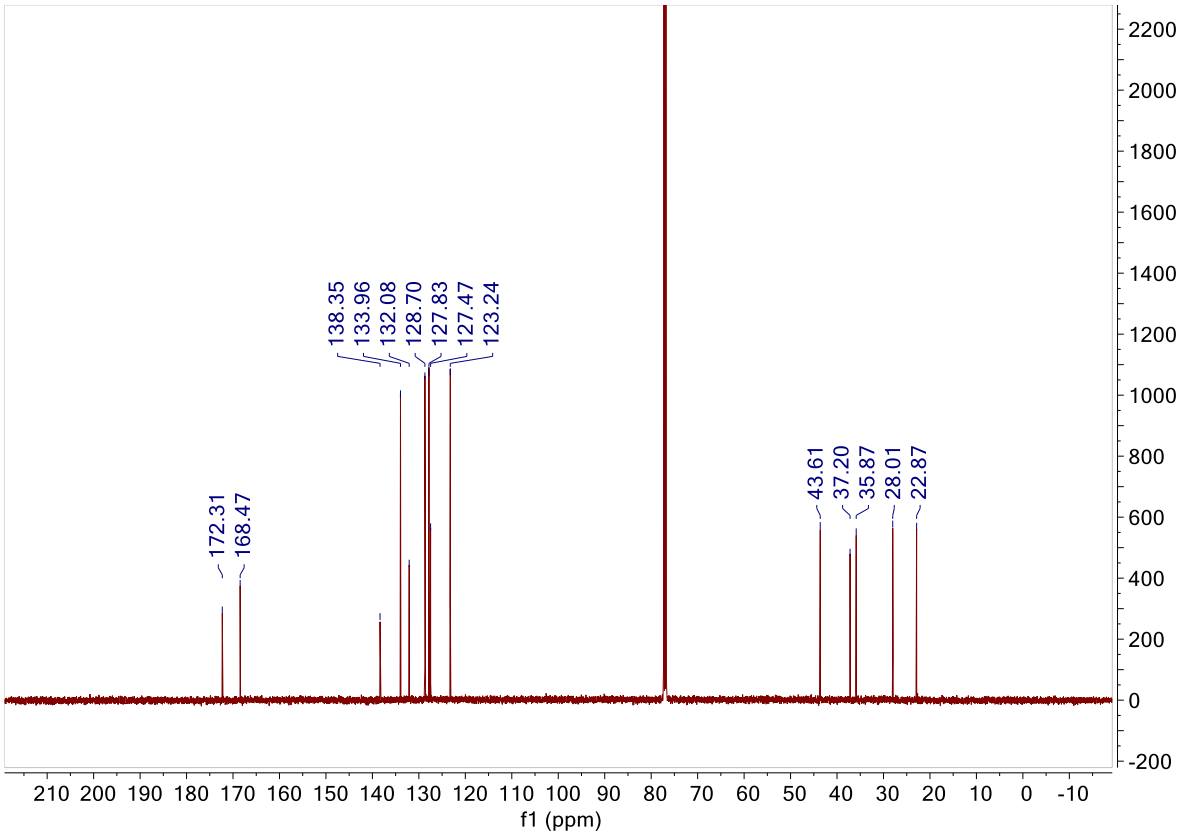




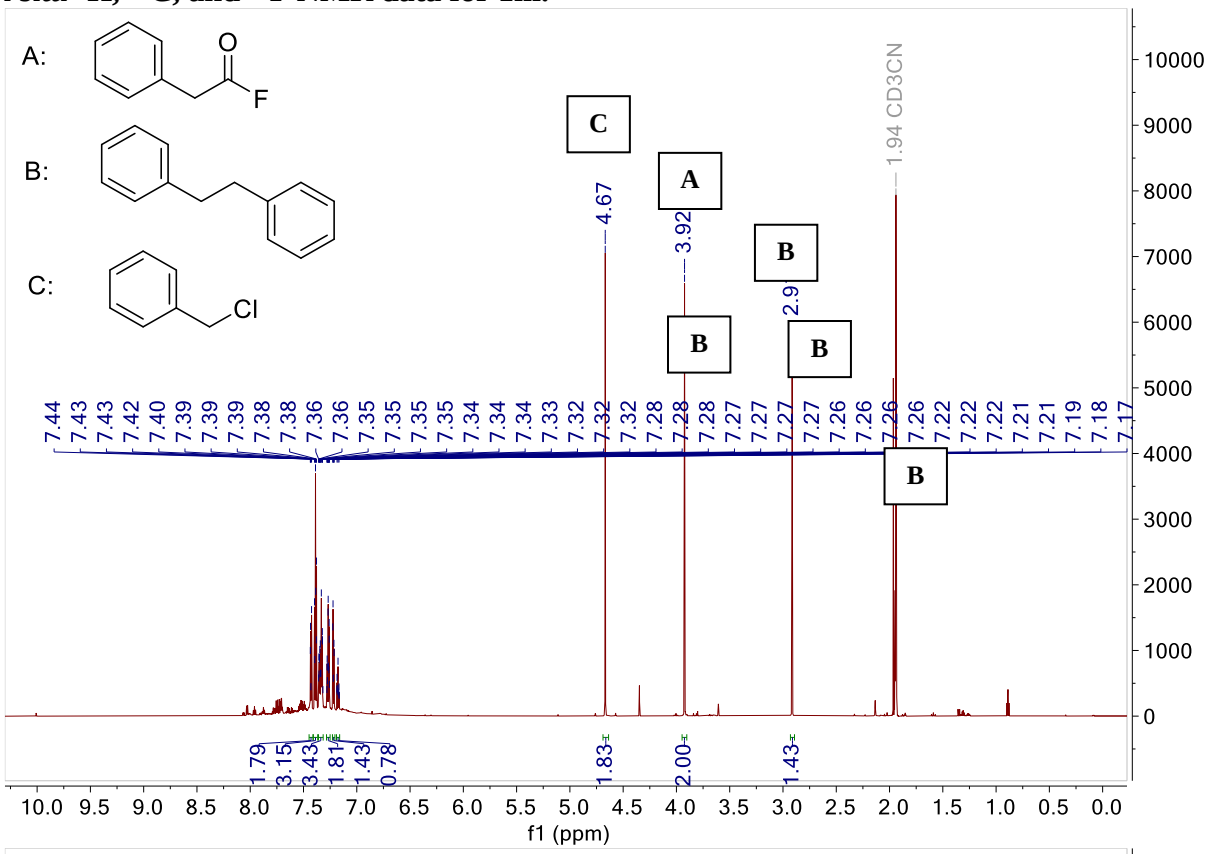

42.99
380
360
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
110
90
70
50
30
10
-10
-30
-50
-70
-90
-110
f1 (ppm)

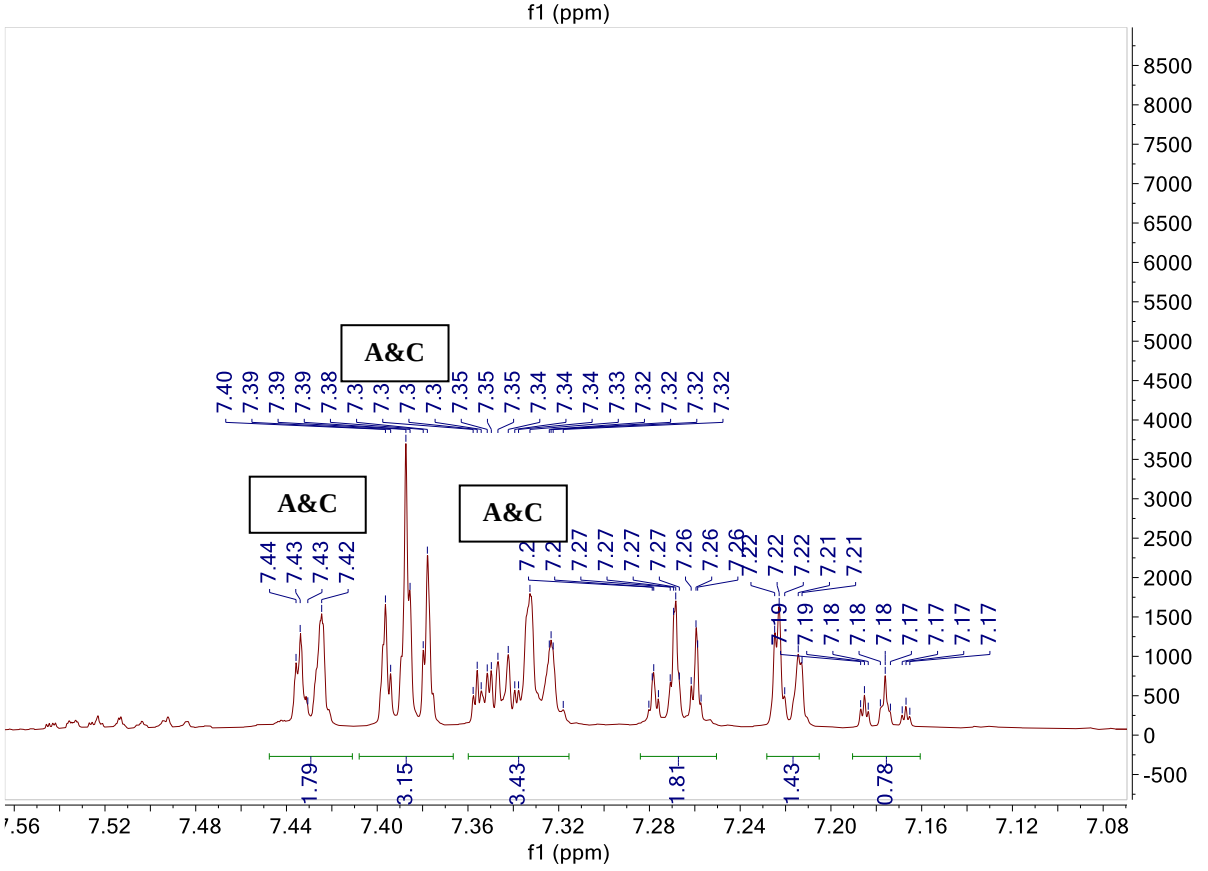
^{1}H and ^{13}C NMR data for 5hhh.

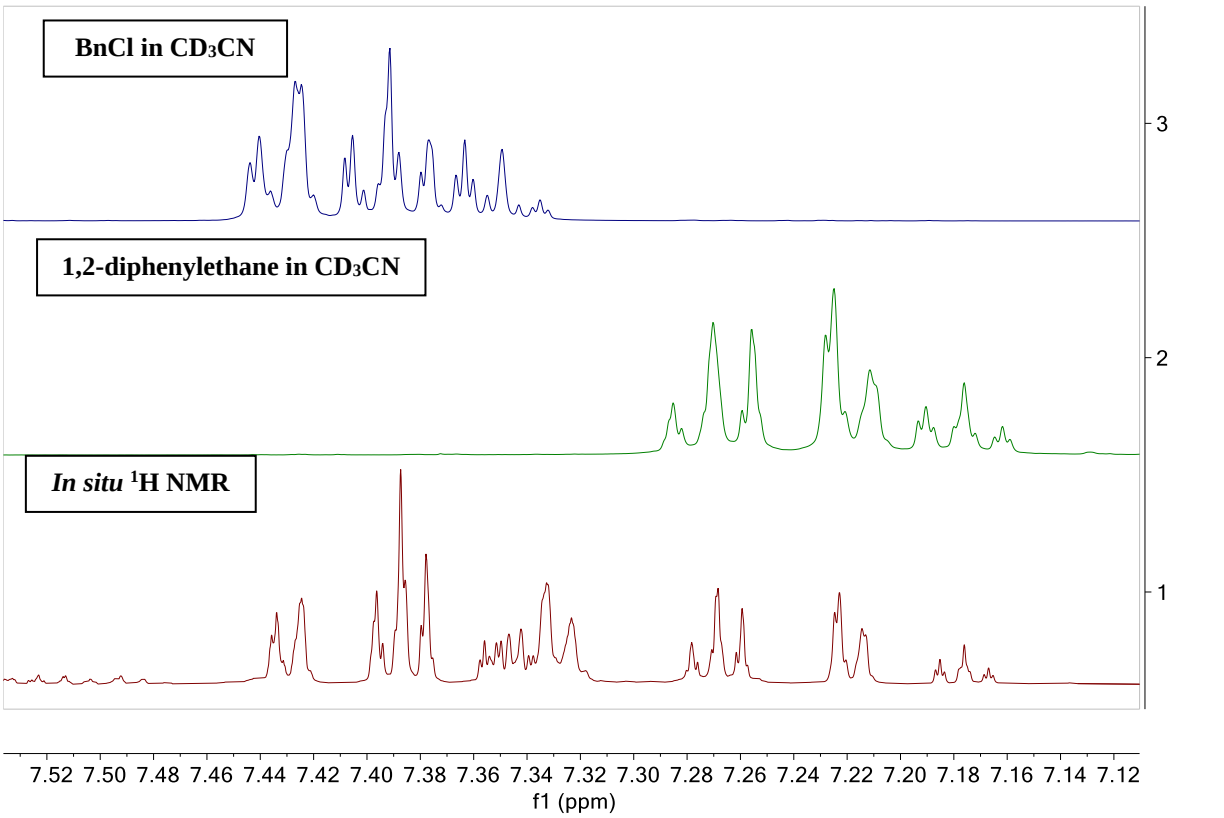


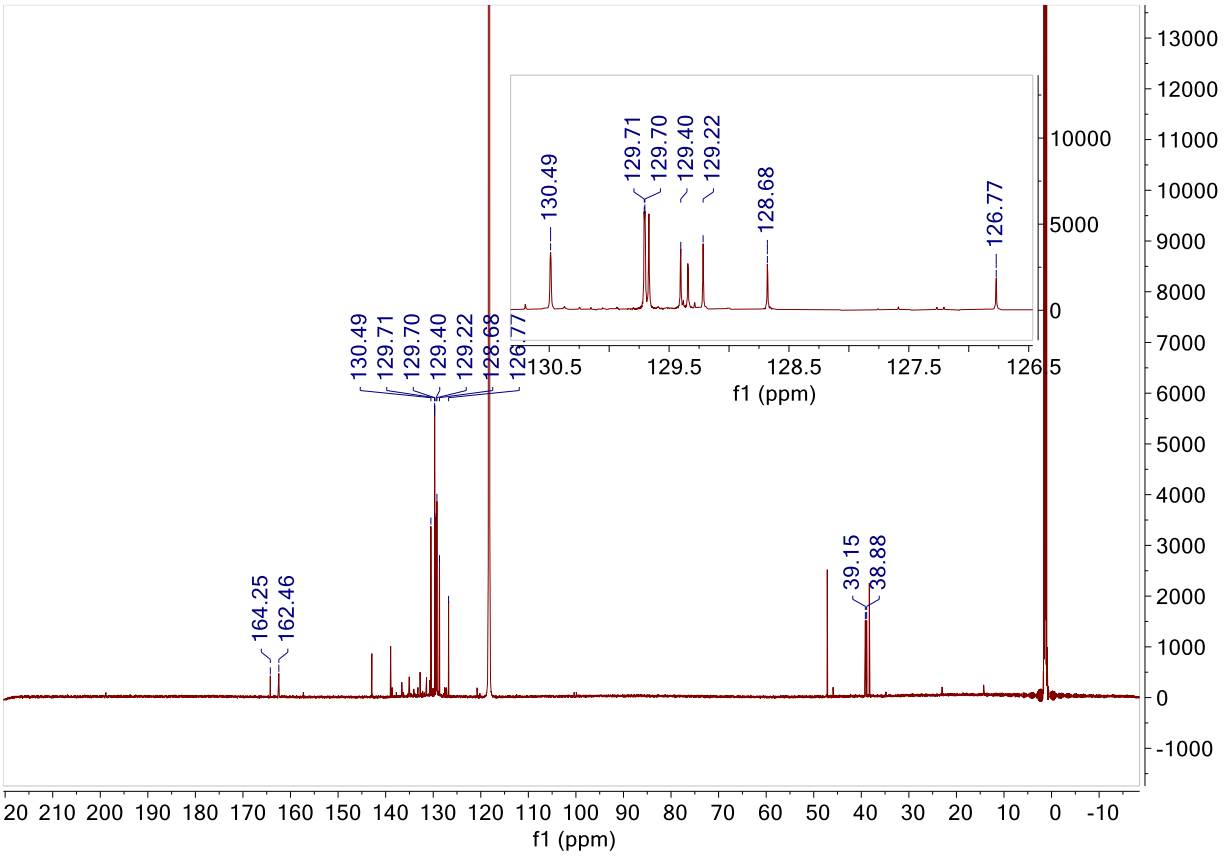


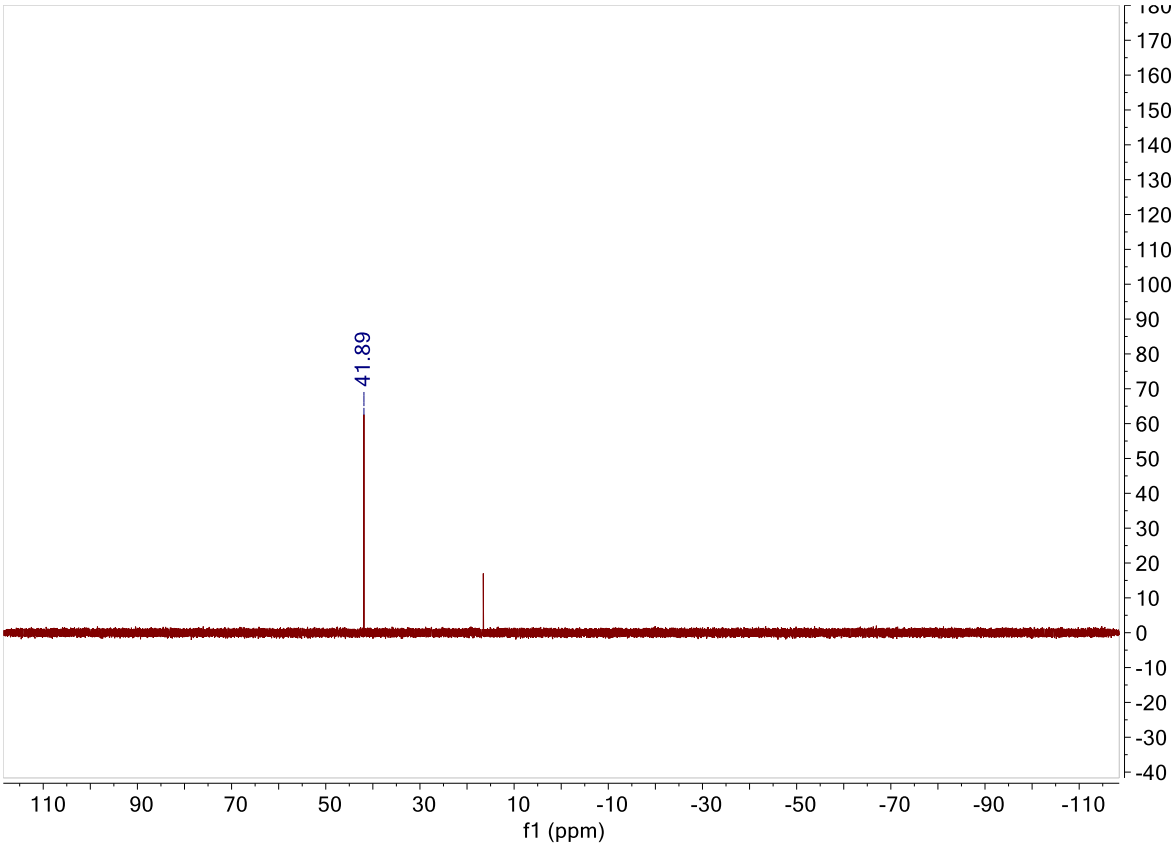
***In situ* ^{1}H, ^{13}C, and ^{19}F NMR data for 1iii.**



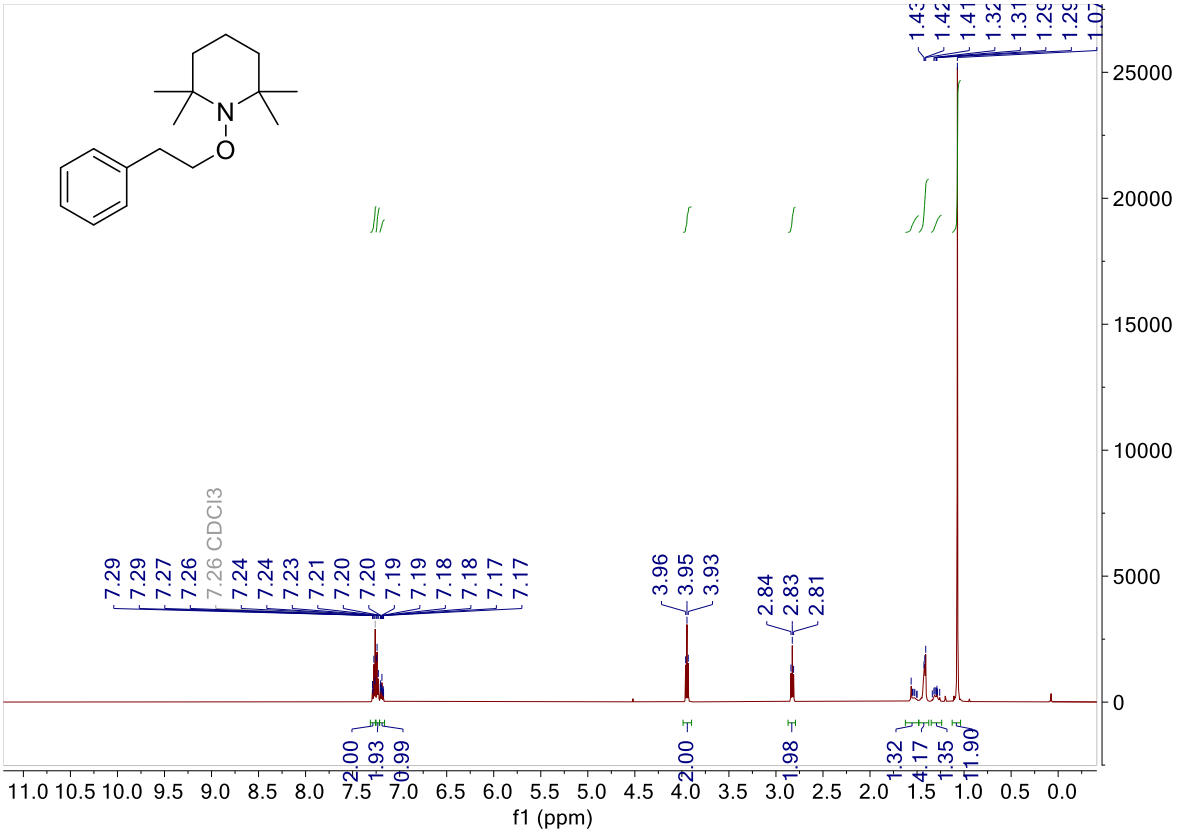


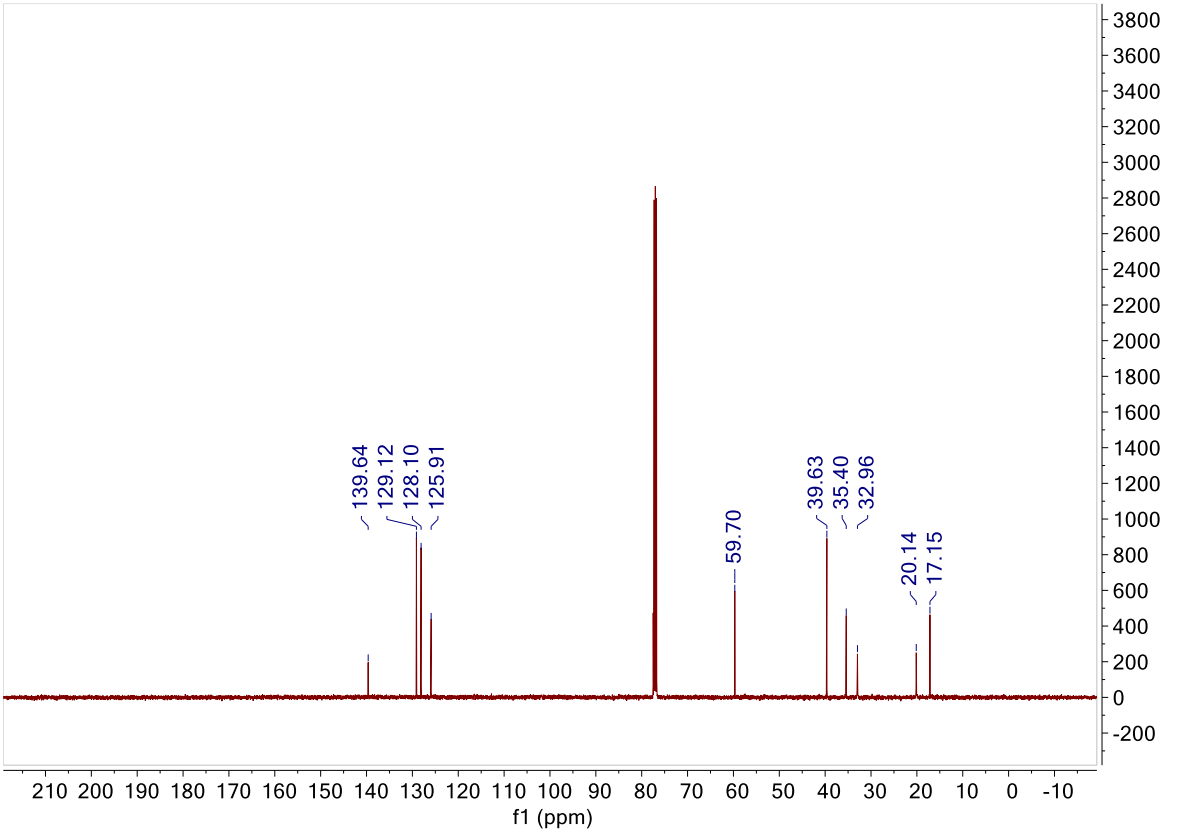

BnCl in CD3CN
1,2-diphenylethane in CD3CN
In situ 1H NMR
3
2
1
7.52 7.50 7.48 7.46 7.44 7.42 7.40 7.38 7.36 7.34 7.32 7.30 7.28 7.26 7.24 7.22 7.20 7.18 7.16 7.14 7.12
f1 (ppm)


130.49
129.71
129.70
129.40
129.22
128.68
126.77
164.25
162.46
39.15
38.88
130.5
129.5
128.5
127.5
126.5
f1 (ppm)
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

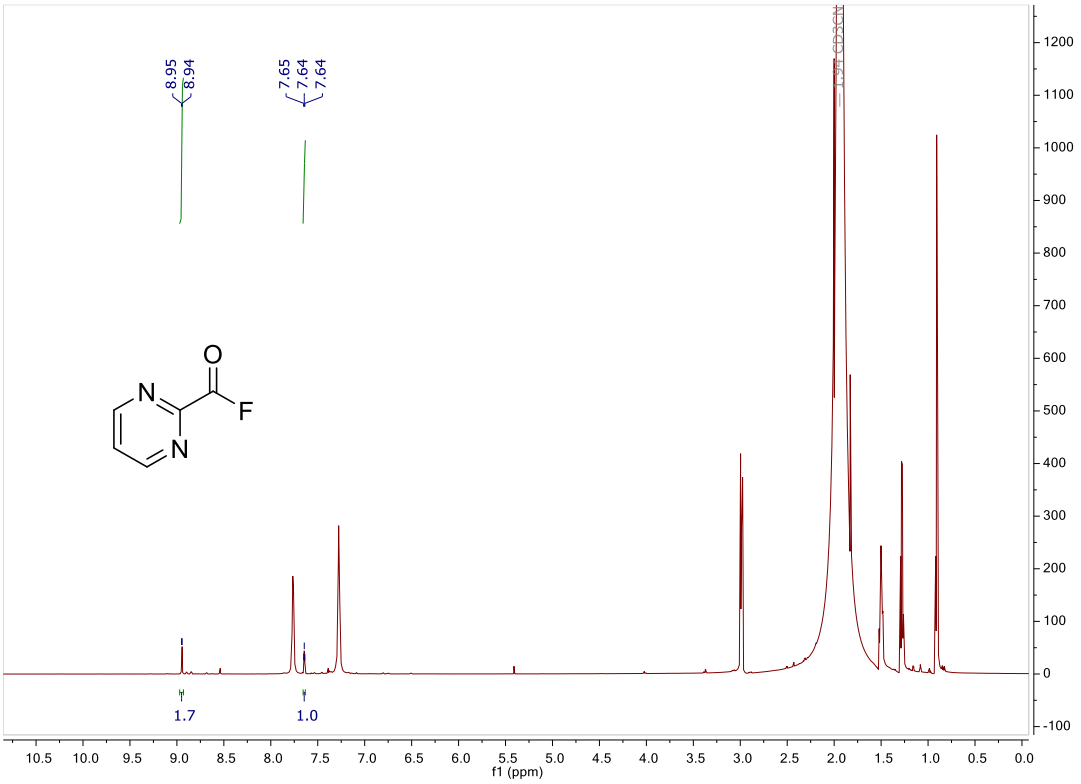

41.89
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
110
90
70
50
30
10
-10
-30
-50
-70
-90
-110
f1 (ppm)

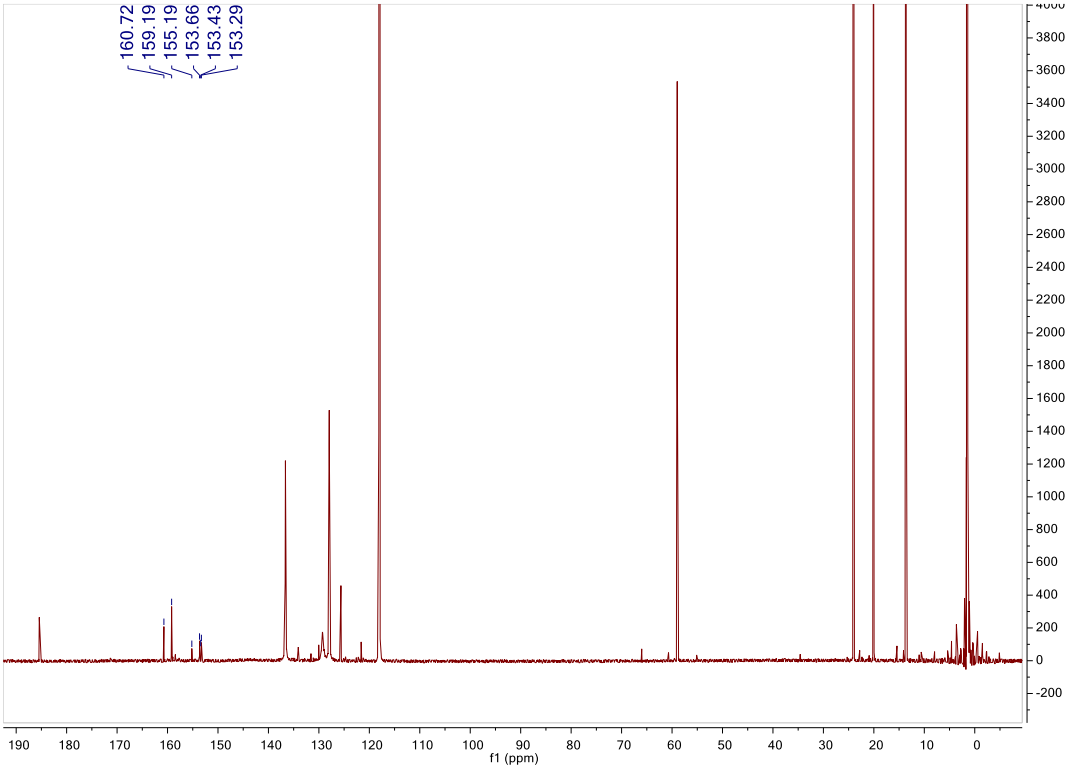
^{1}H and ^{13}C NMR data for 3.

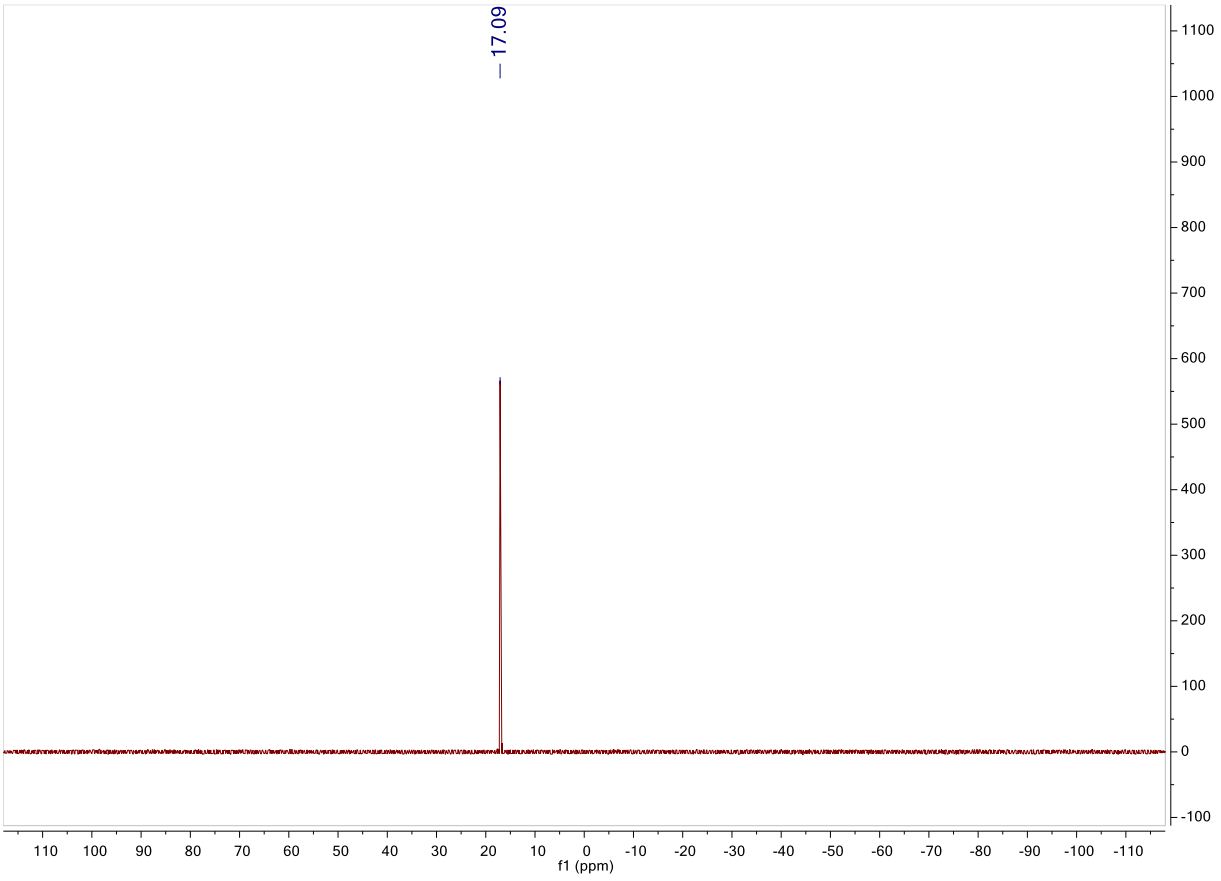




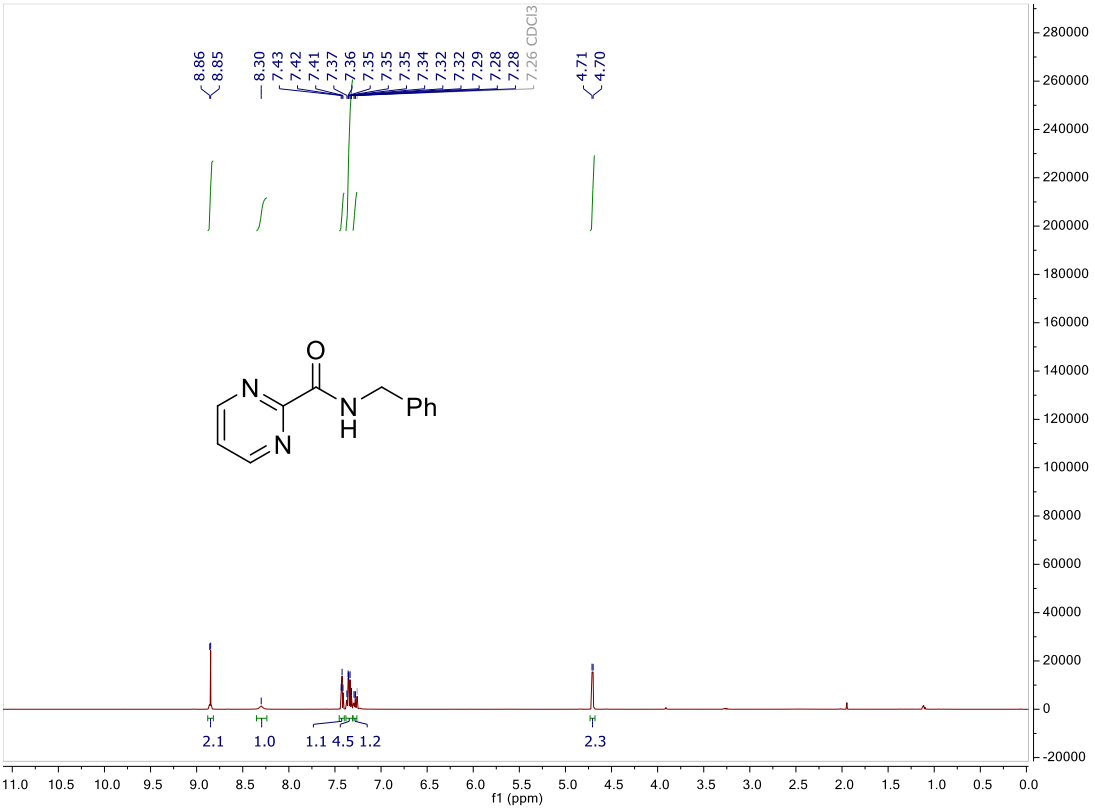
In situ ^{1}H, ^{13}C, and ^{19}F NMR data for 4a

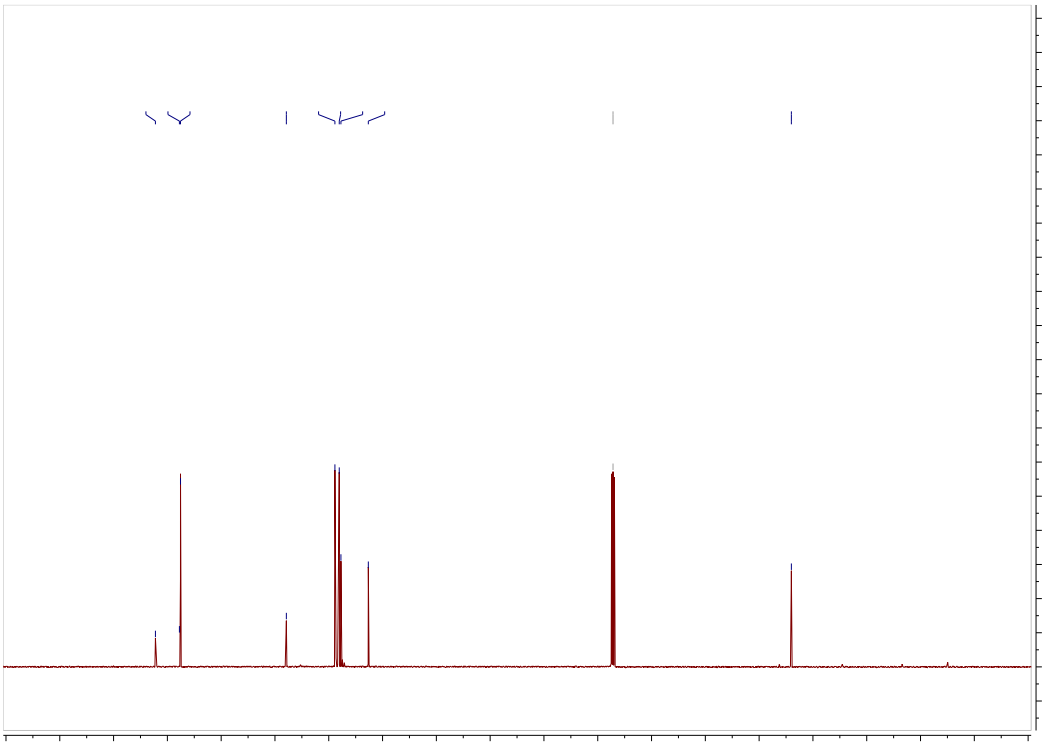




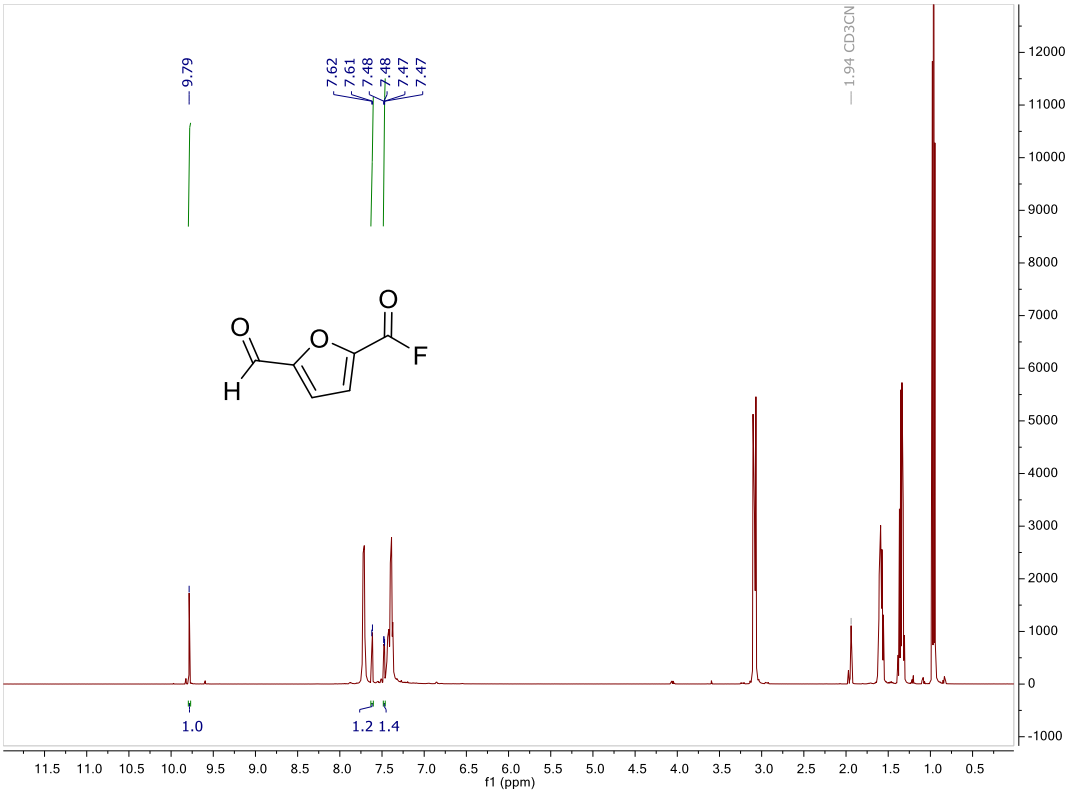

17.09
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110
f1 (ppm)

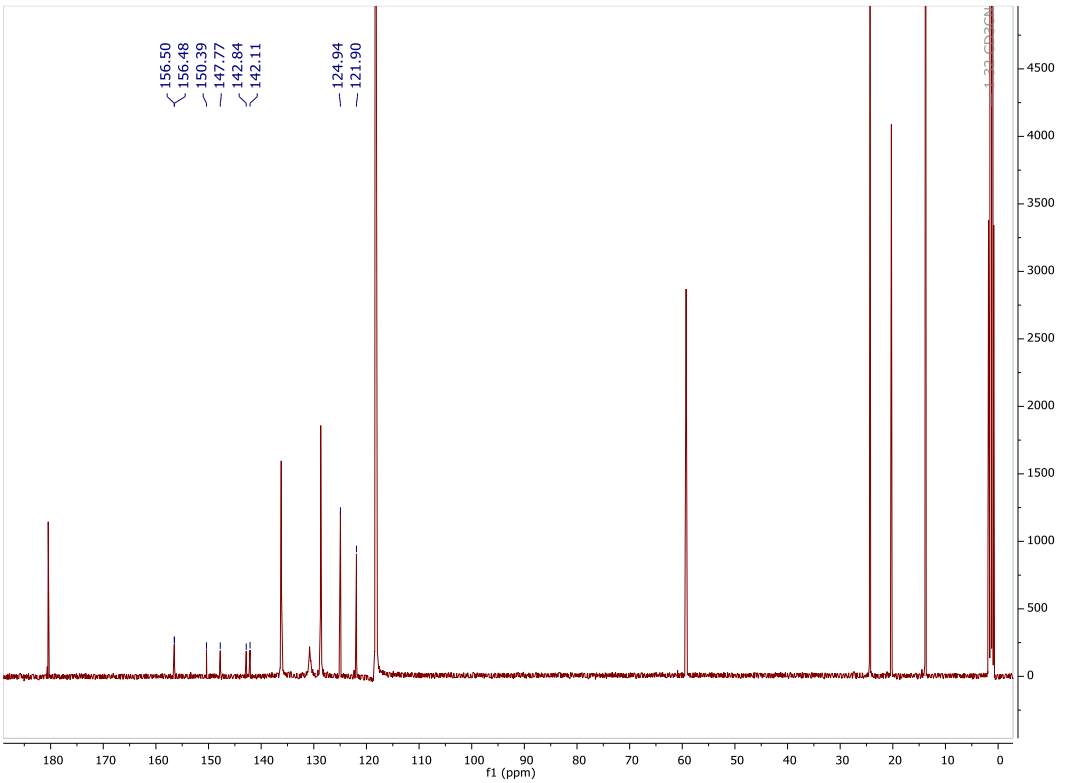
^{1}H and ^{13}C NMR data for 7a

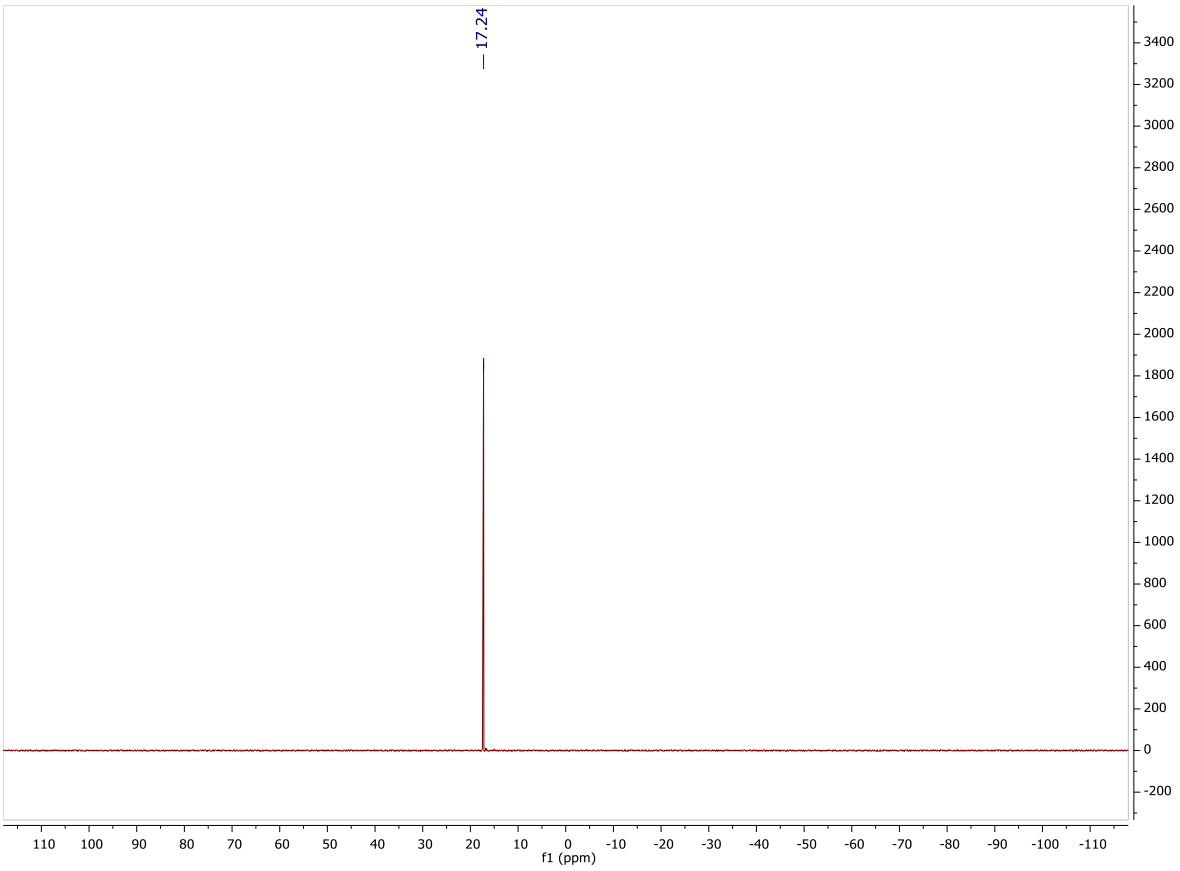




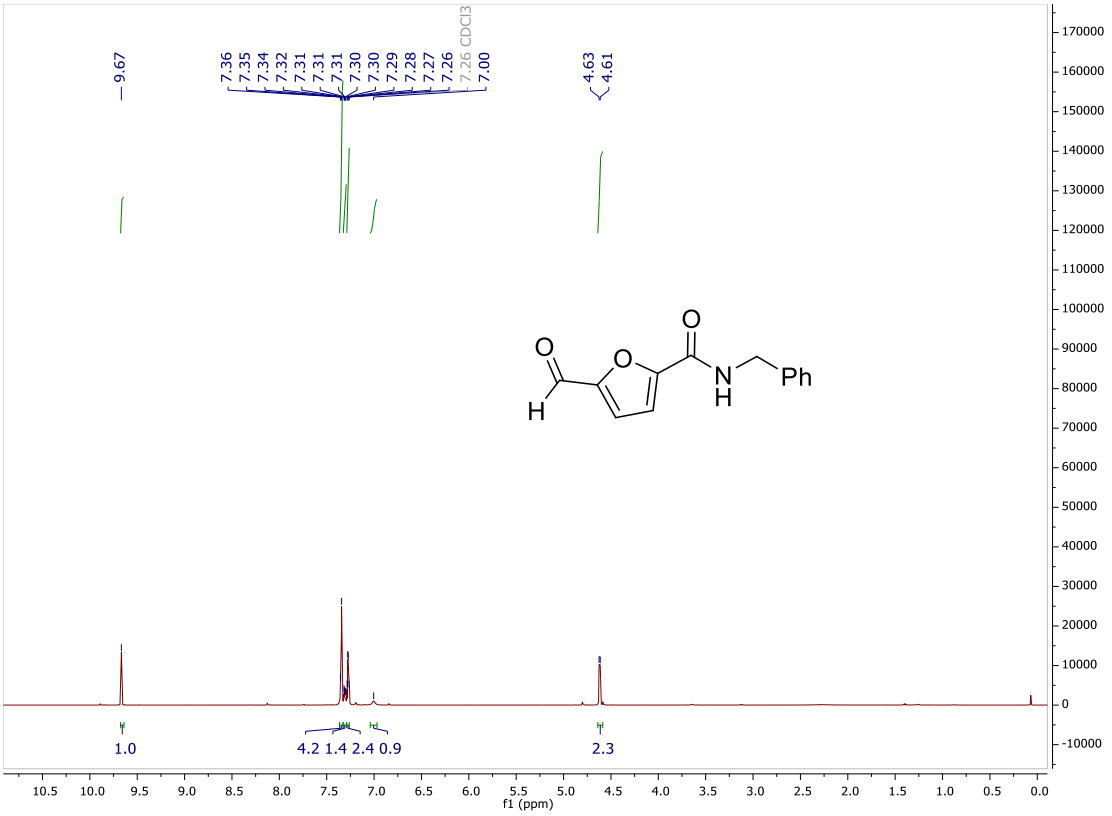
In situ ^{1}H, ^{13}C, and ^{19}F NMR data for 4b

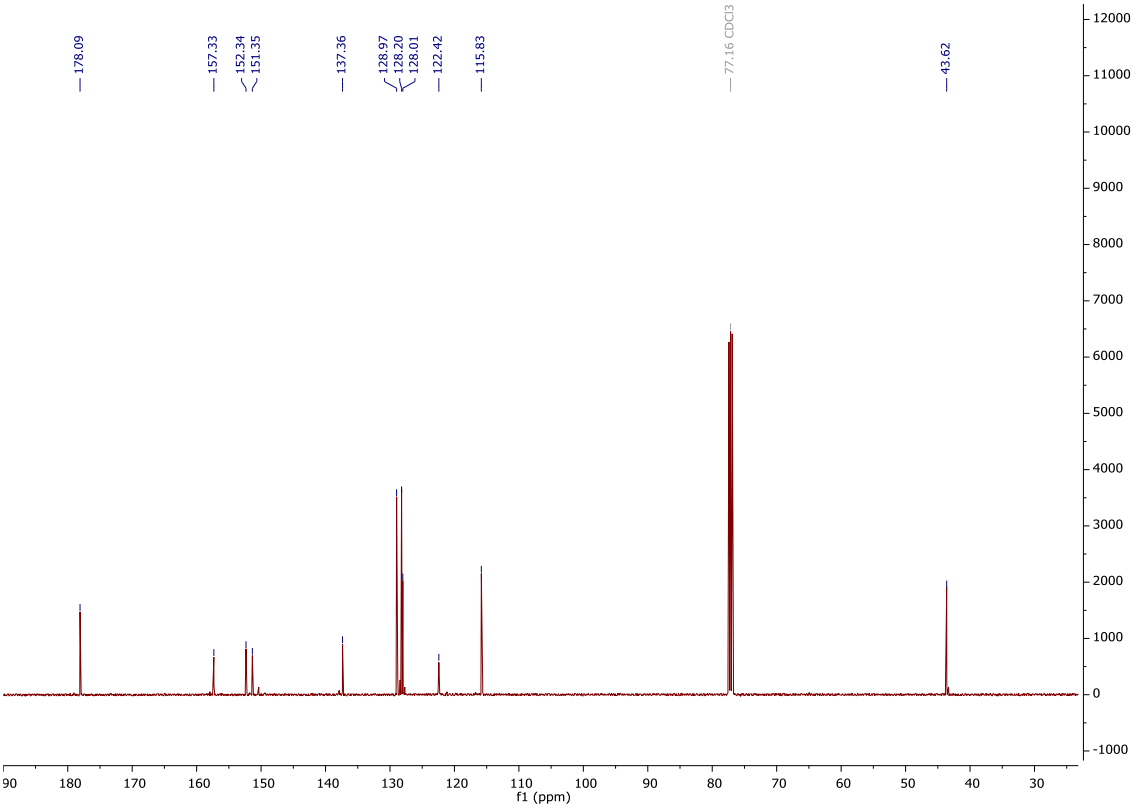




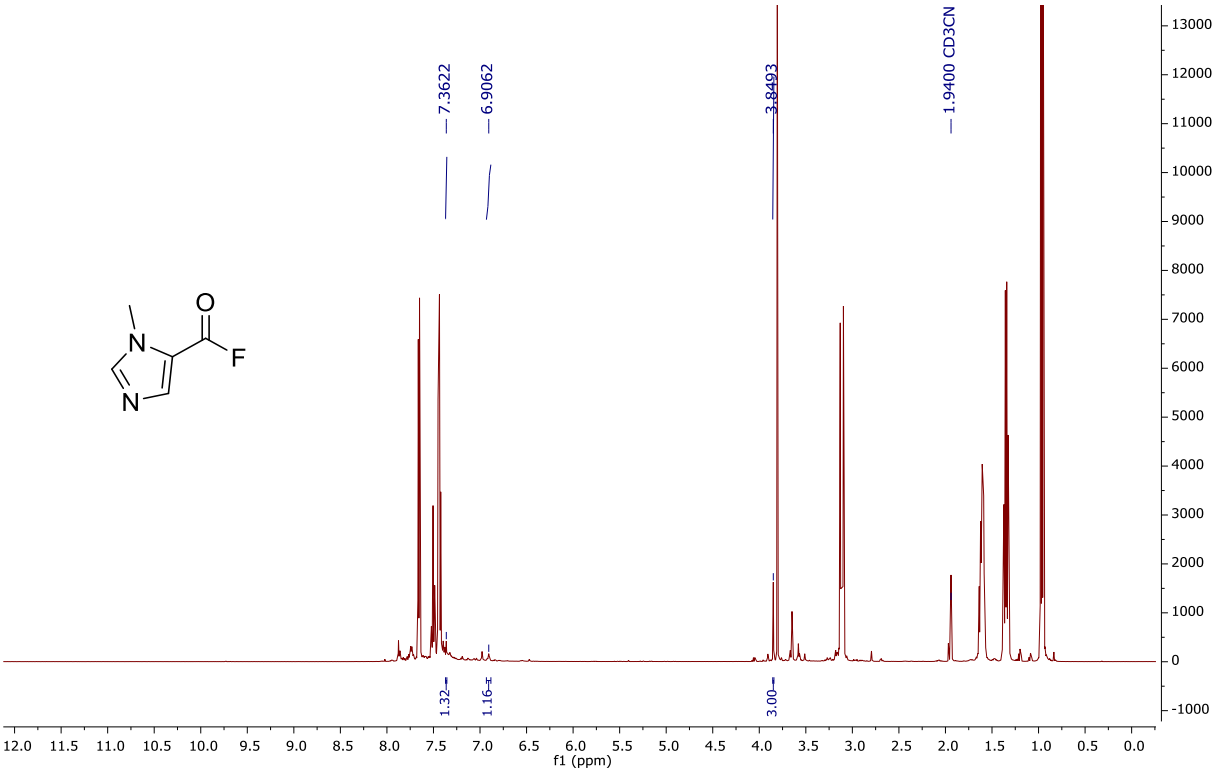

17.24
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110
f1 (ppm)

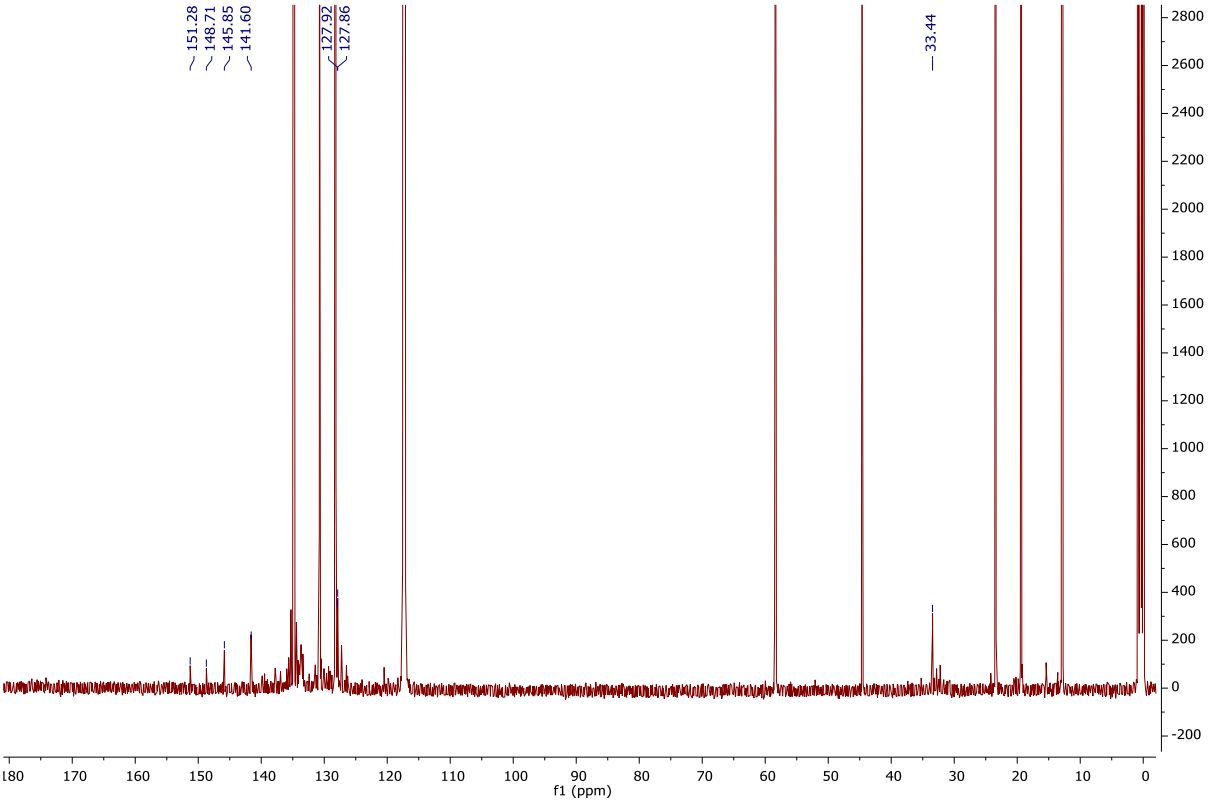
^{1}H and ^{13}C NMR data for 7b

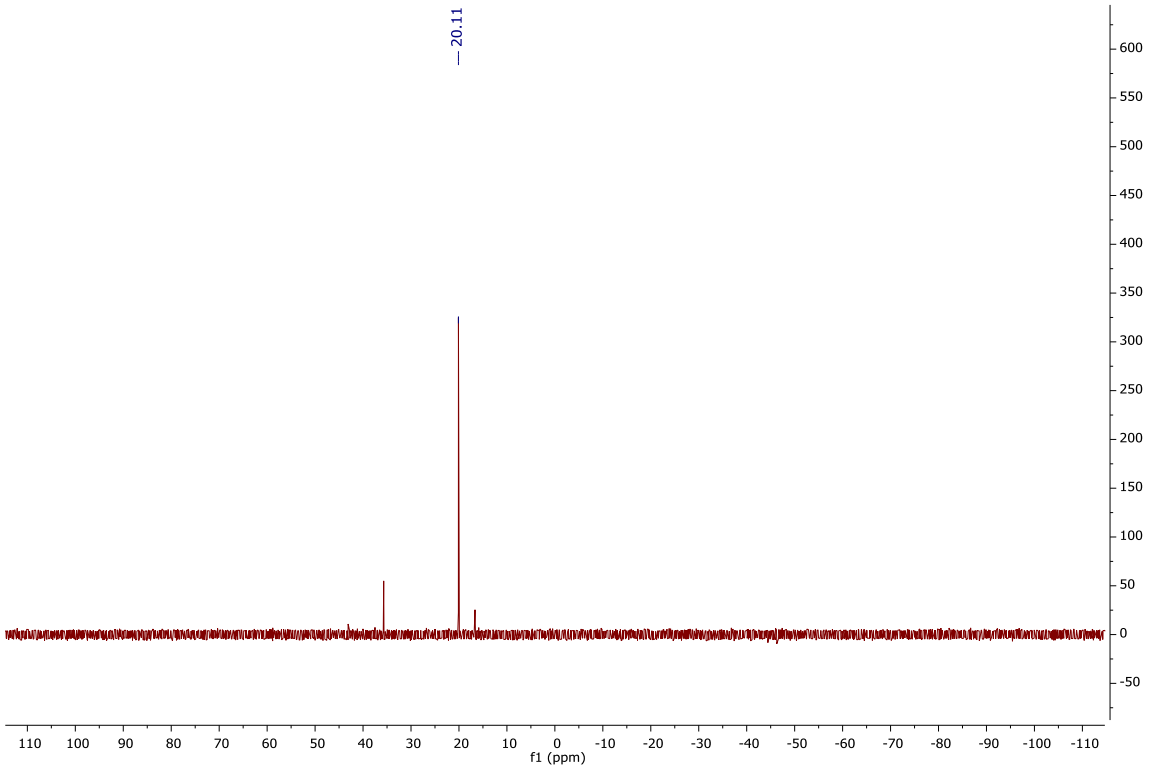




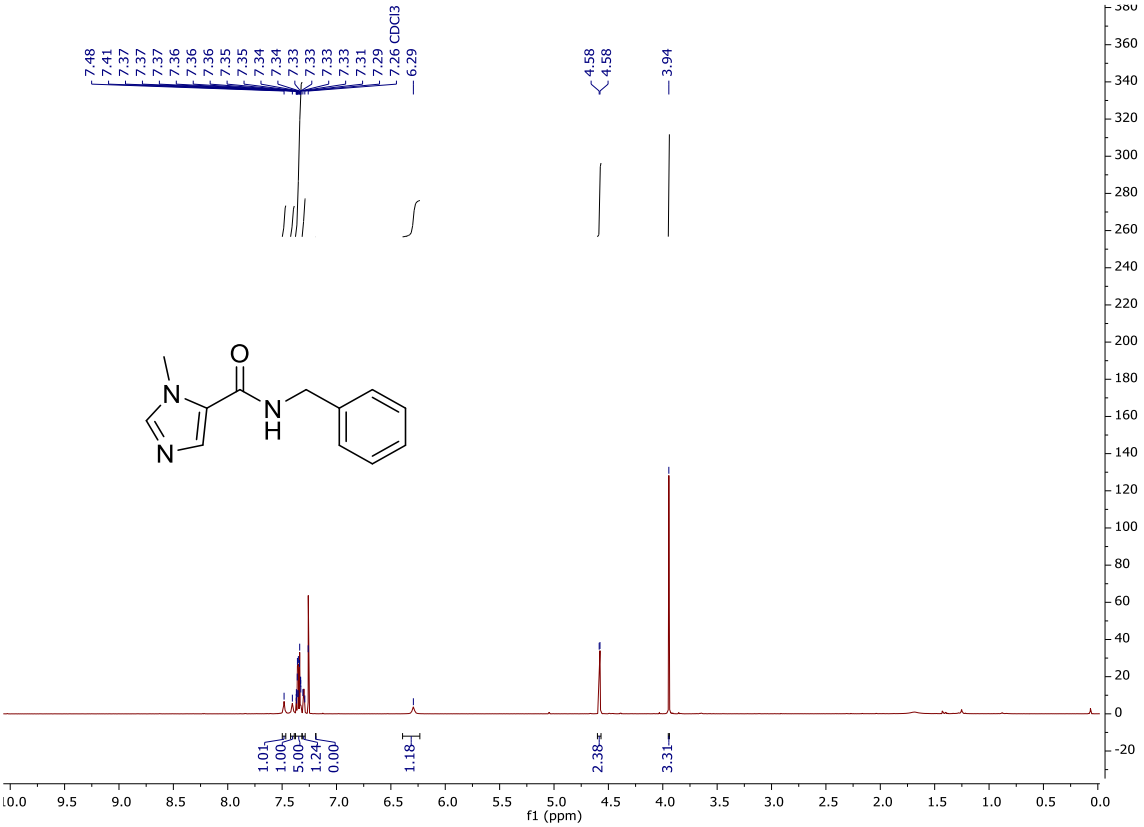
In situ ^{1}H, ^{13}C, and ^{19}F NMR data for 4c

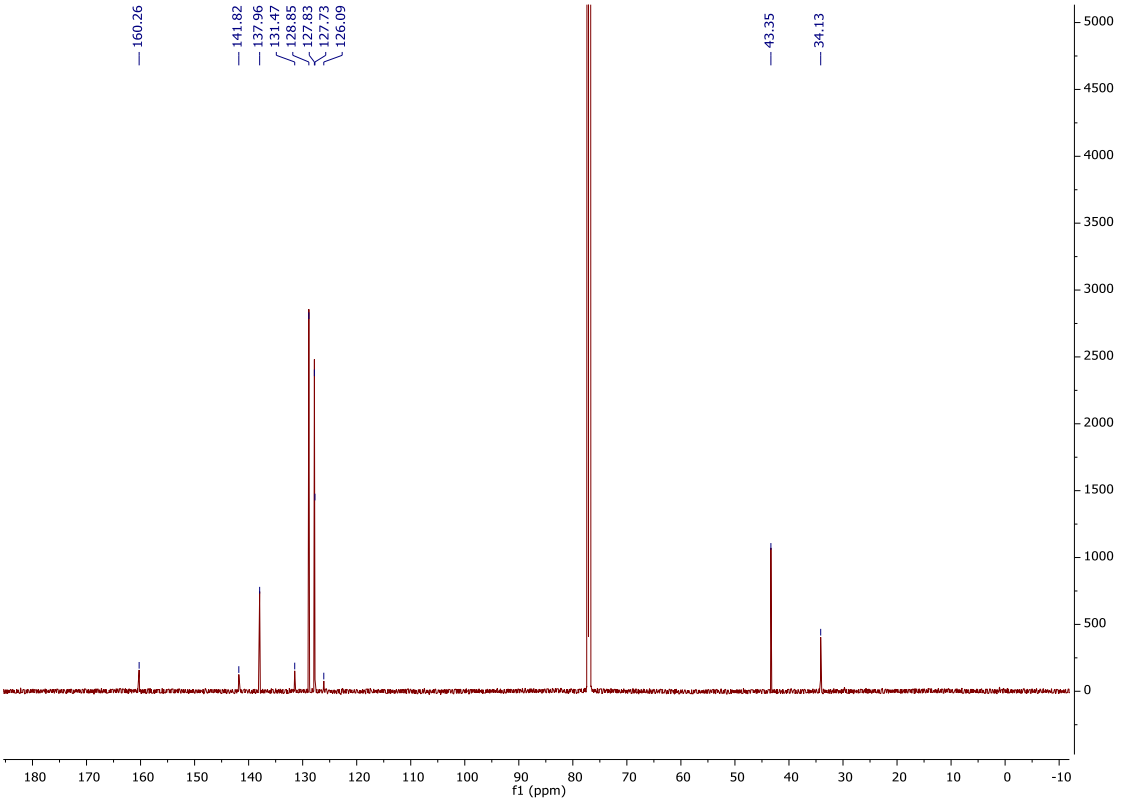




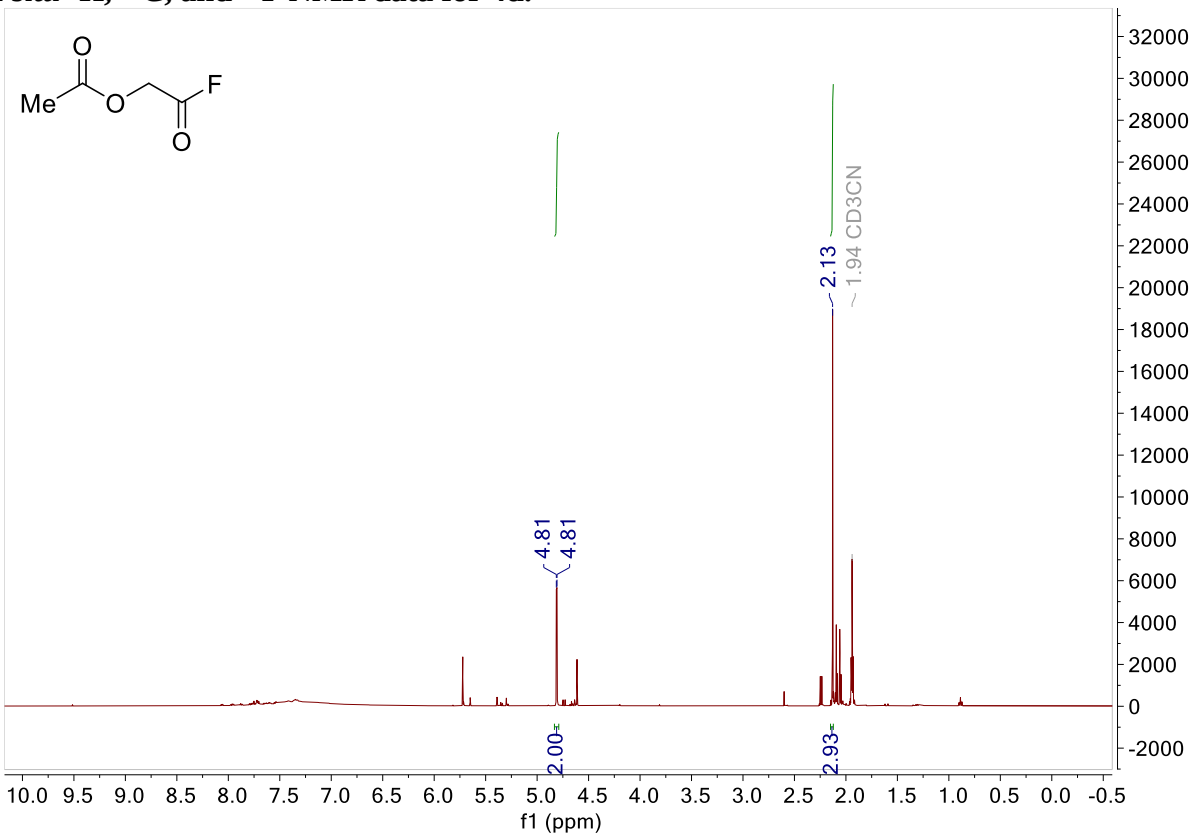

20.11
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110
f1 (ppm)

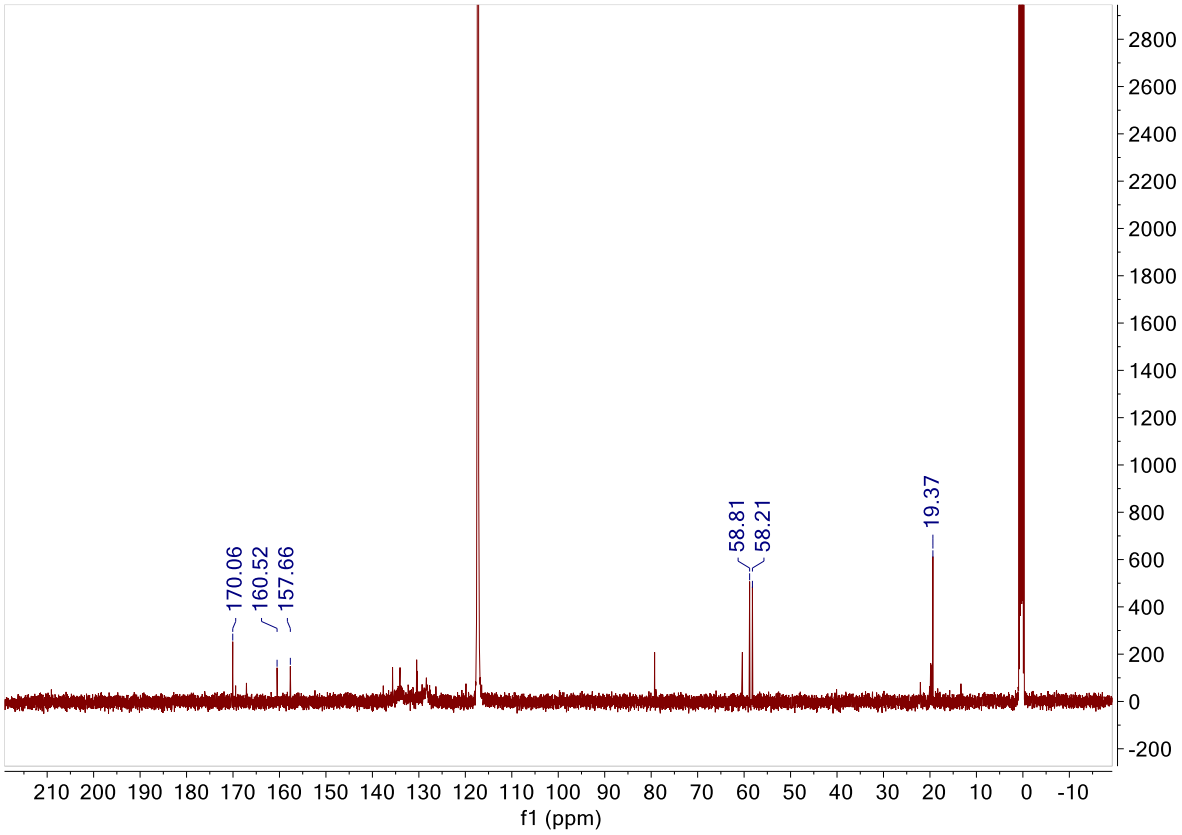
^{1}H and ^{13}C NMR for 7c

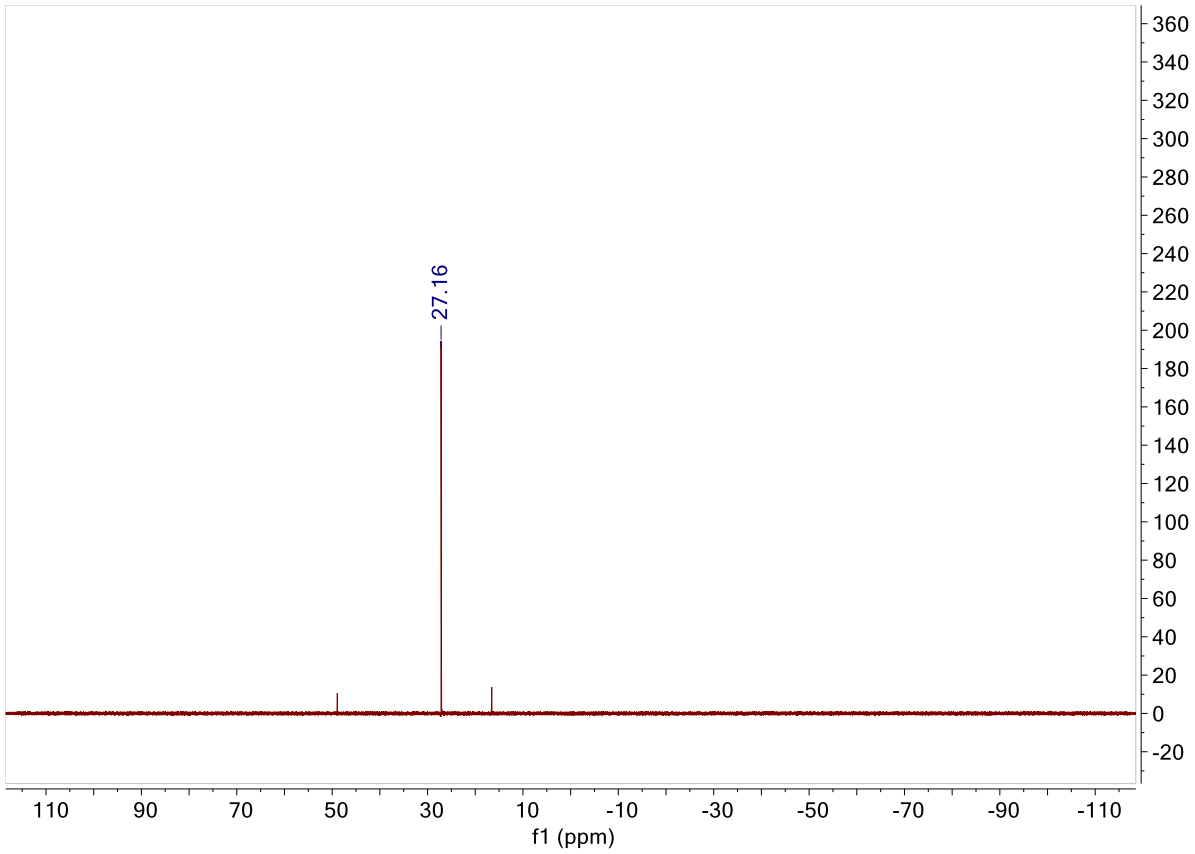




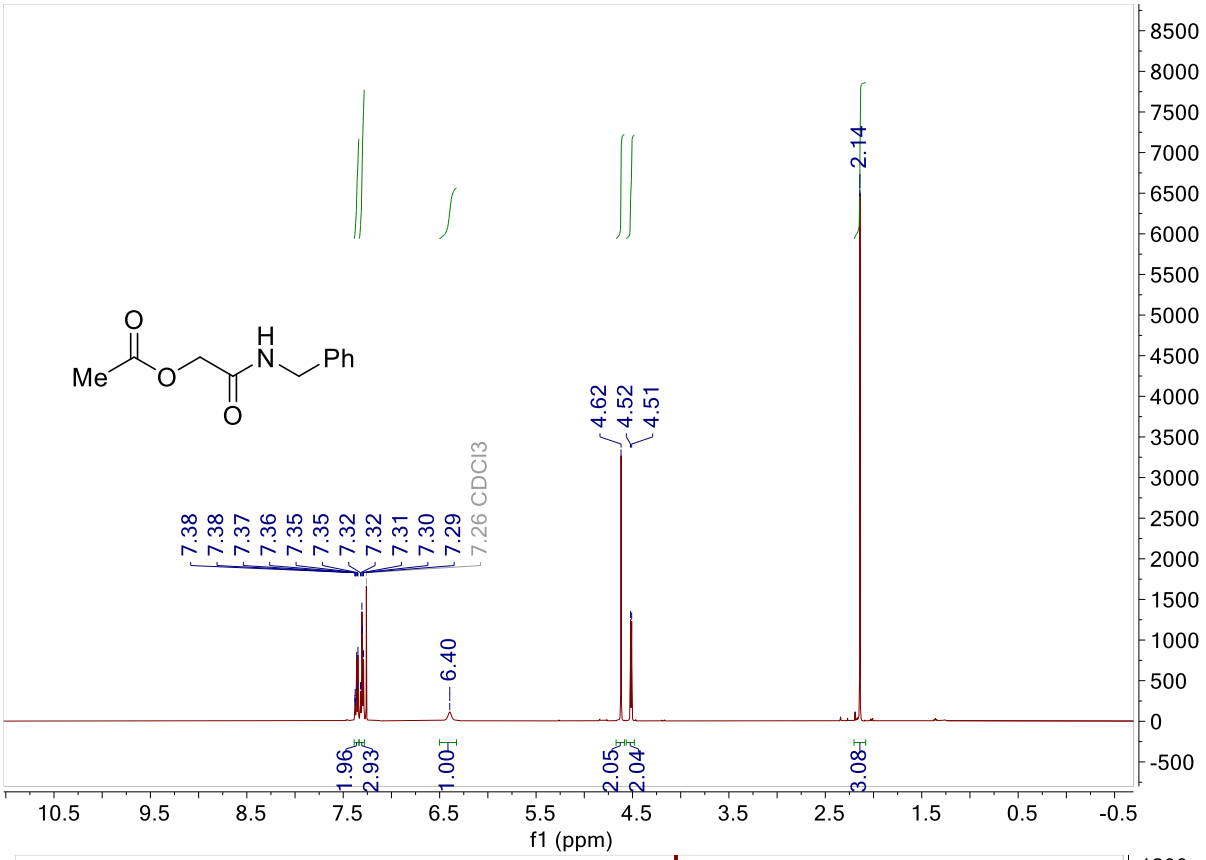
***In situ* ^{1}H, ^{13}C, and ^{19}F NMR data for 4d.**

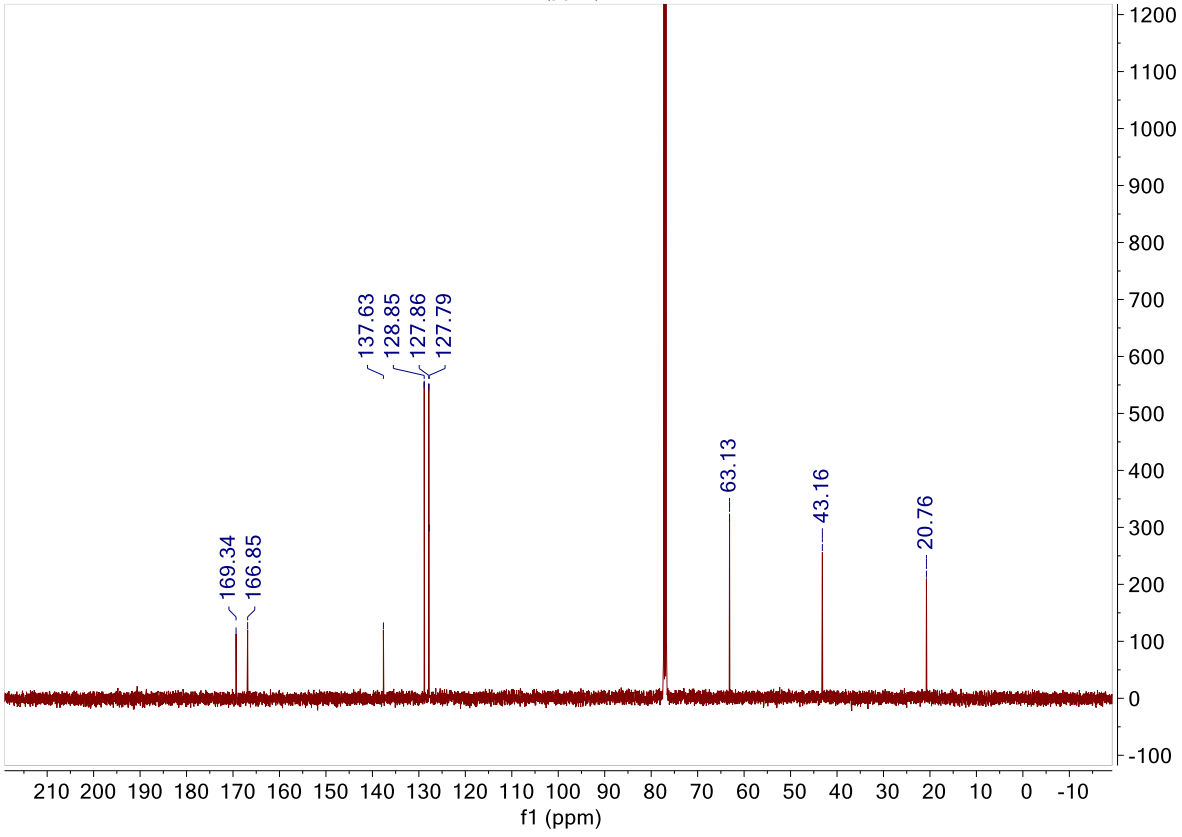




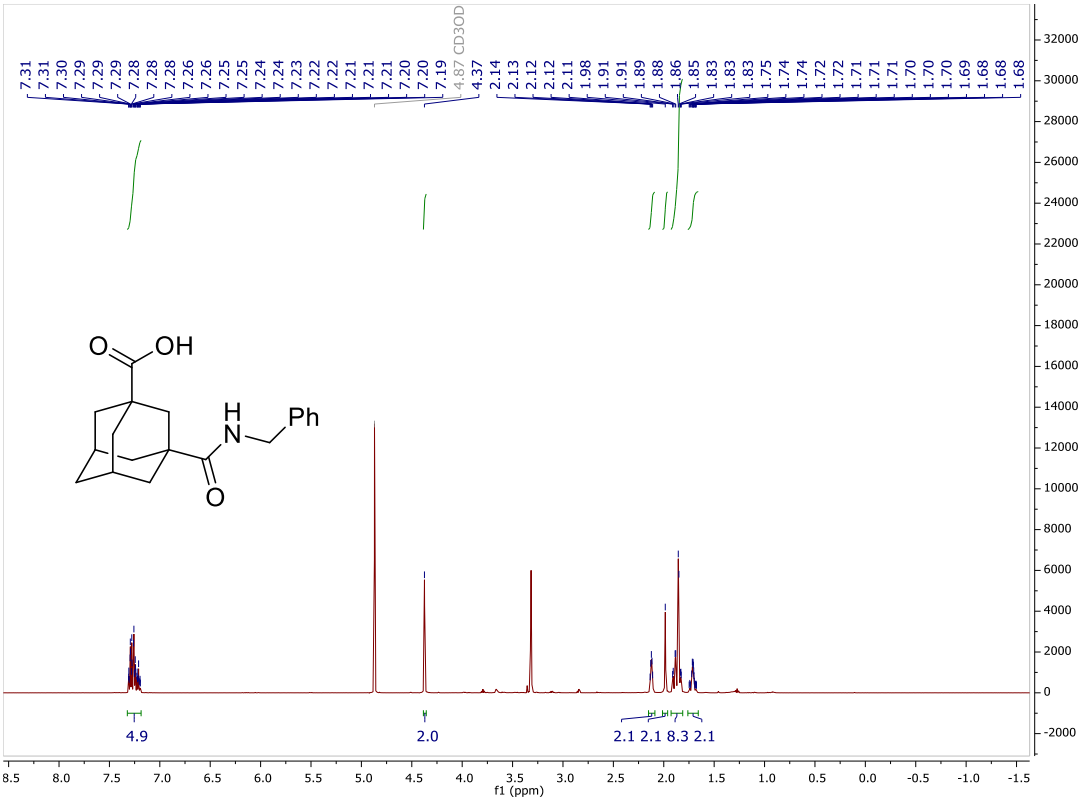

27.16
360
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
110
90
70
50
30
10
-10
-30
-50
-70
-90
-110
f1 (ppm)

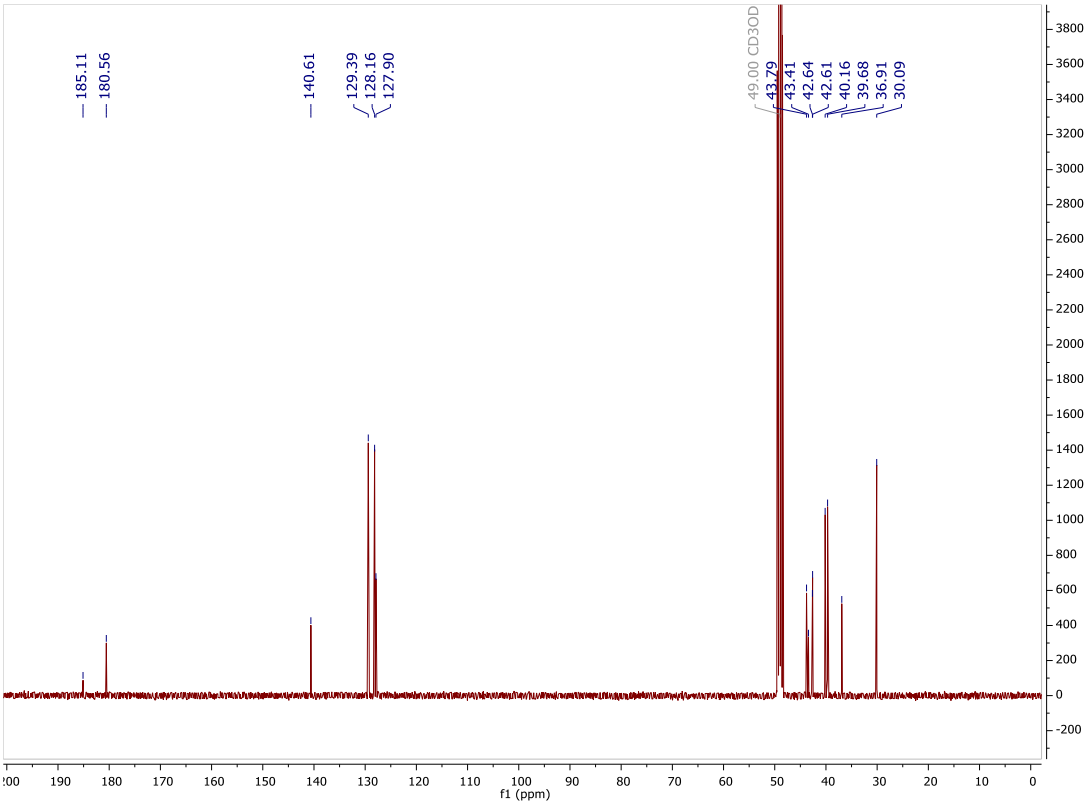
^{1}H and ^{13}C NMR data for 7d.



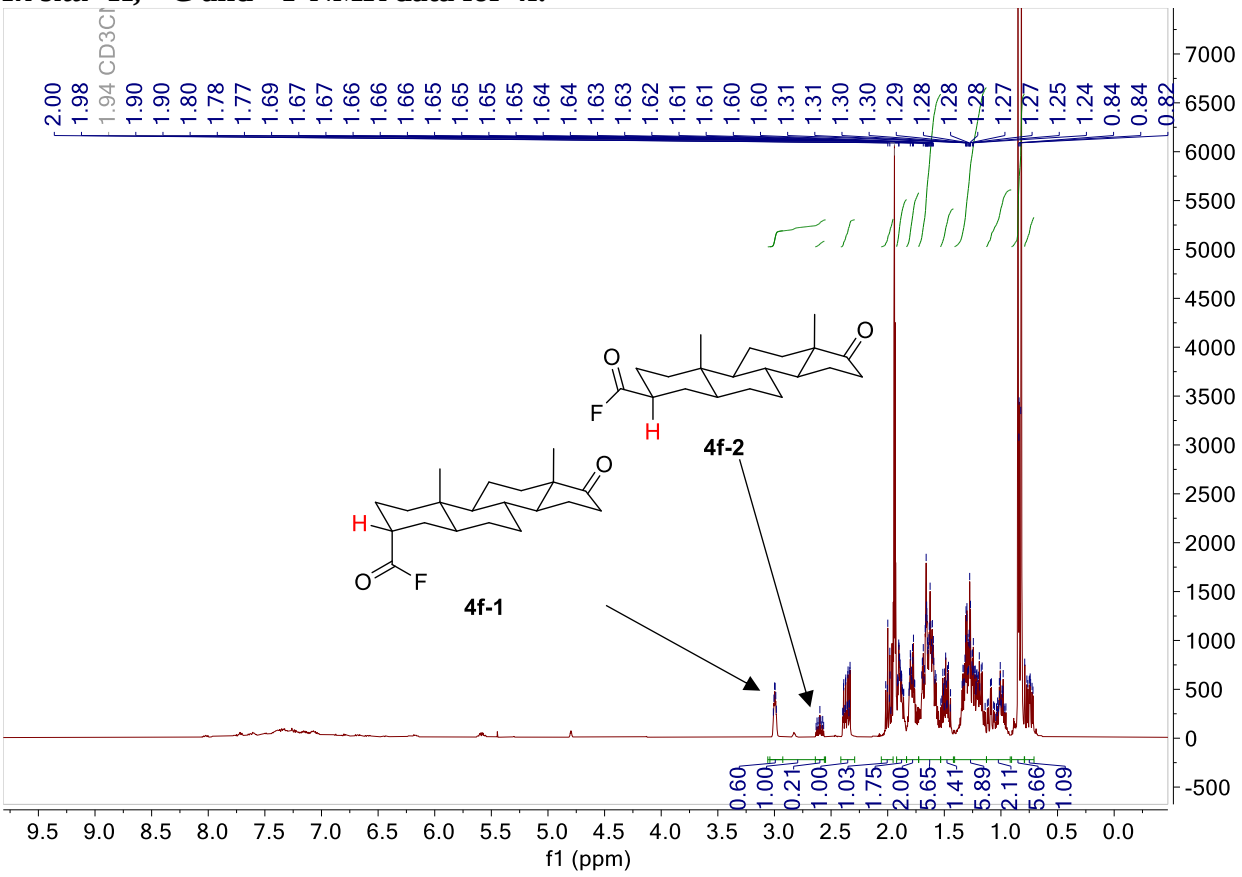


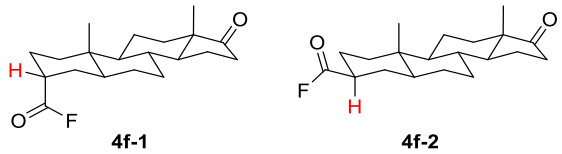
^{1}H and ^{13}C NMR data for 4e

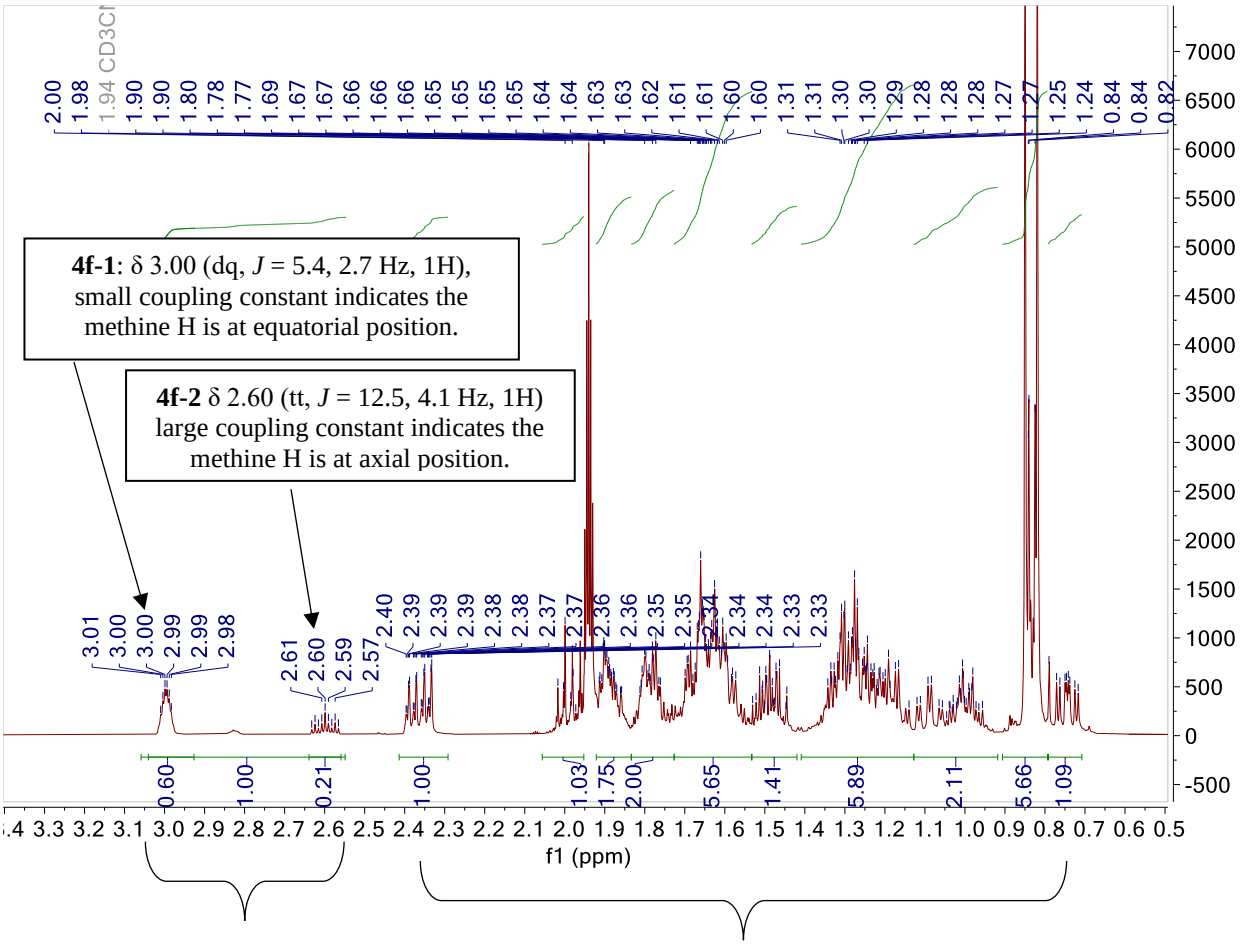




***In situ* ^{1}H, ^{13}C and ^{19}F NMR data for 4f.**





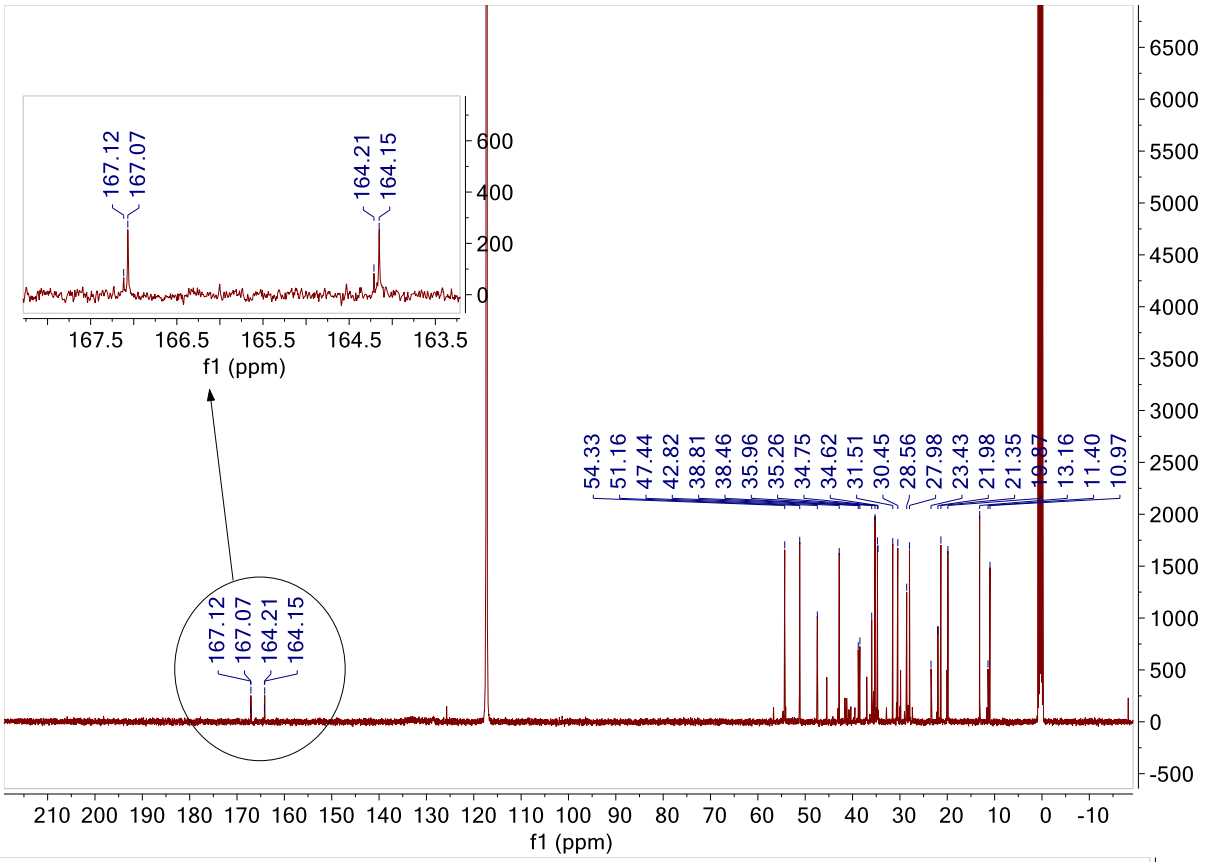


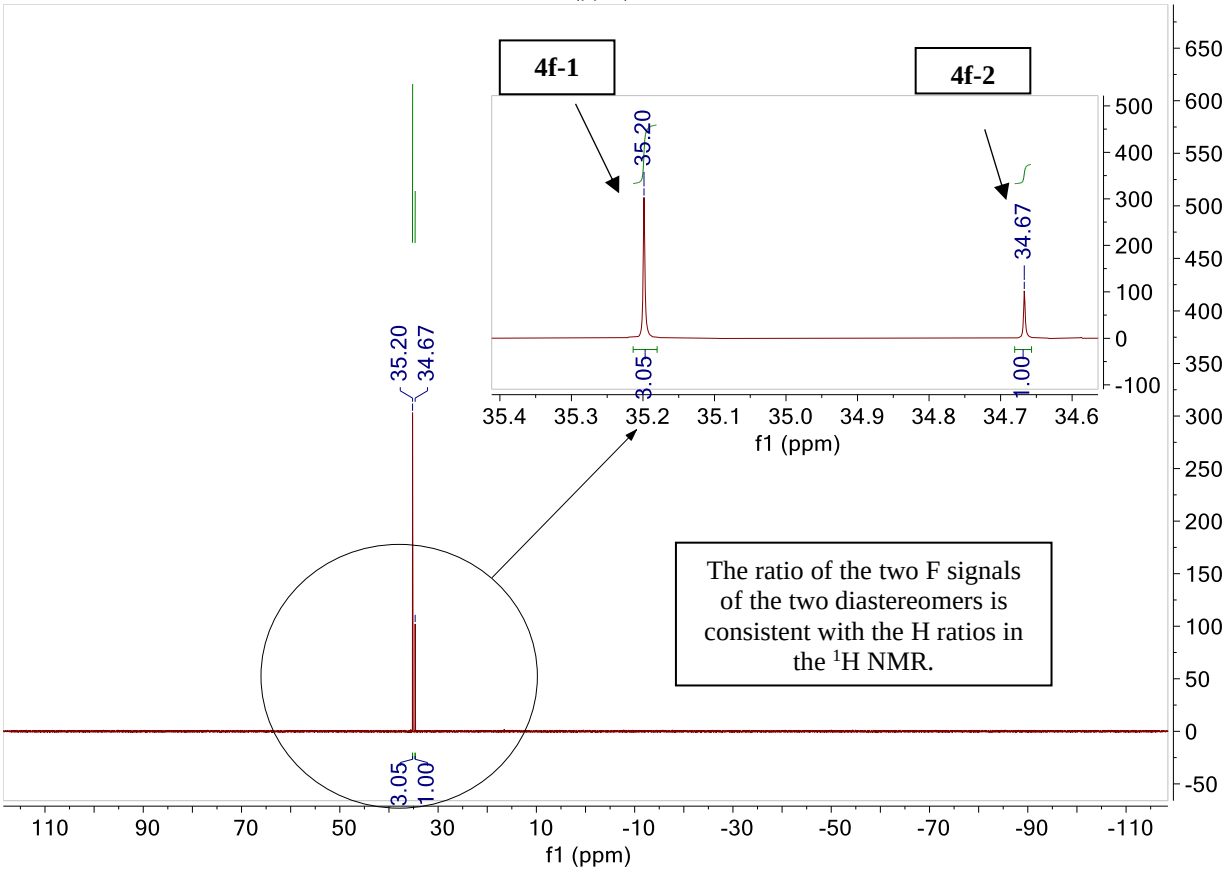
4f-1: δ 3.00 (dq, *J* = 5.4, 2.7 Hz, 1H), small coupling constant indicates the methine H is at equatorial position.

4f-2 δ 2.60 (tt, *J* = 12.5, 4.1 Hz, 1H) large coupling constant indicates the methine H is at axial position.

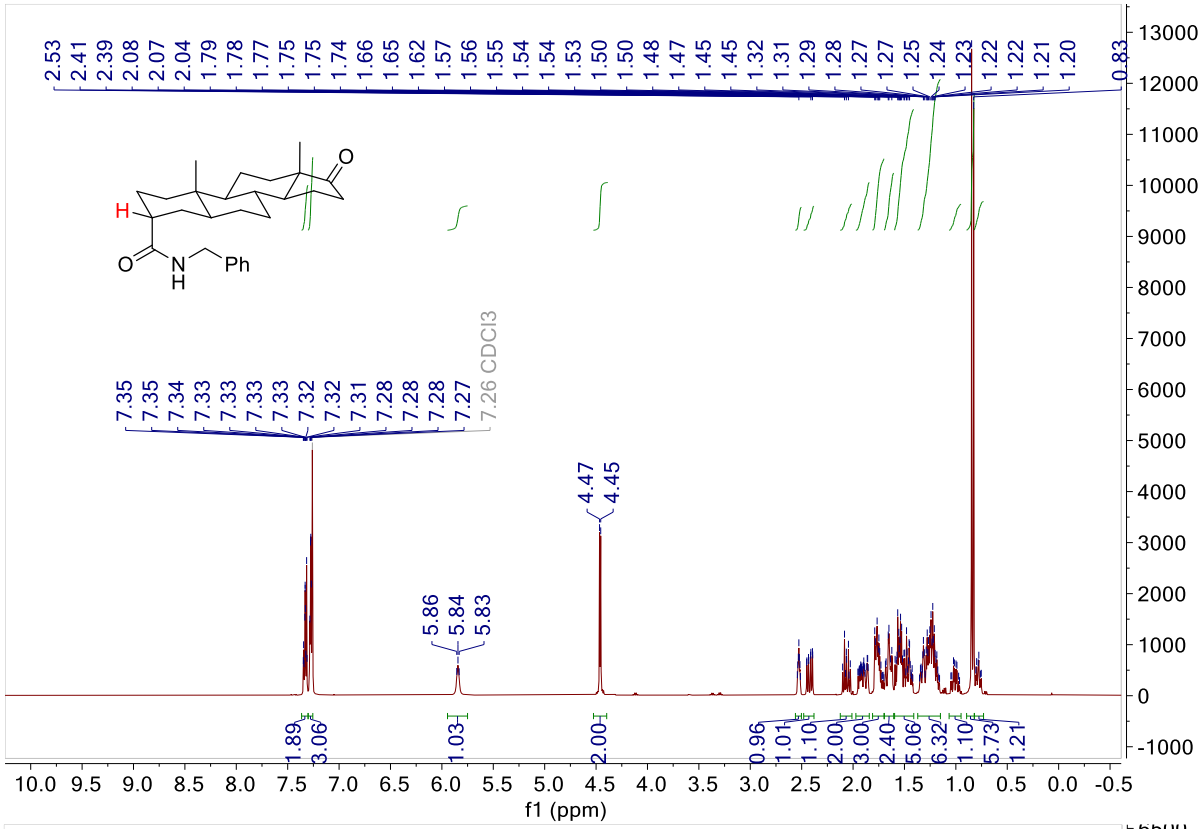
Set the total integration of both methine C-H to one proton.

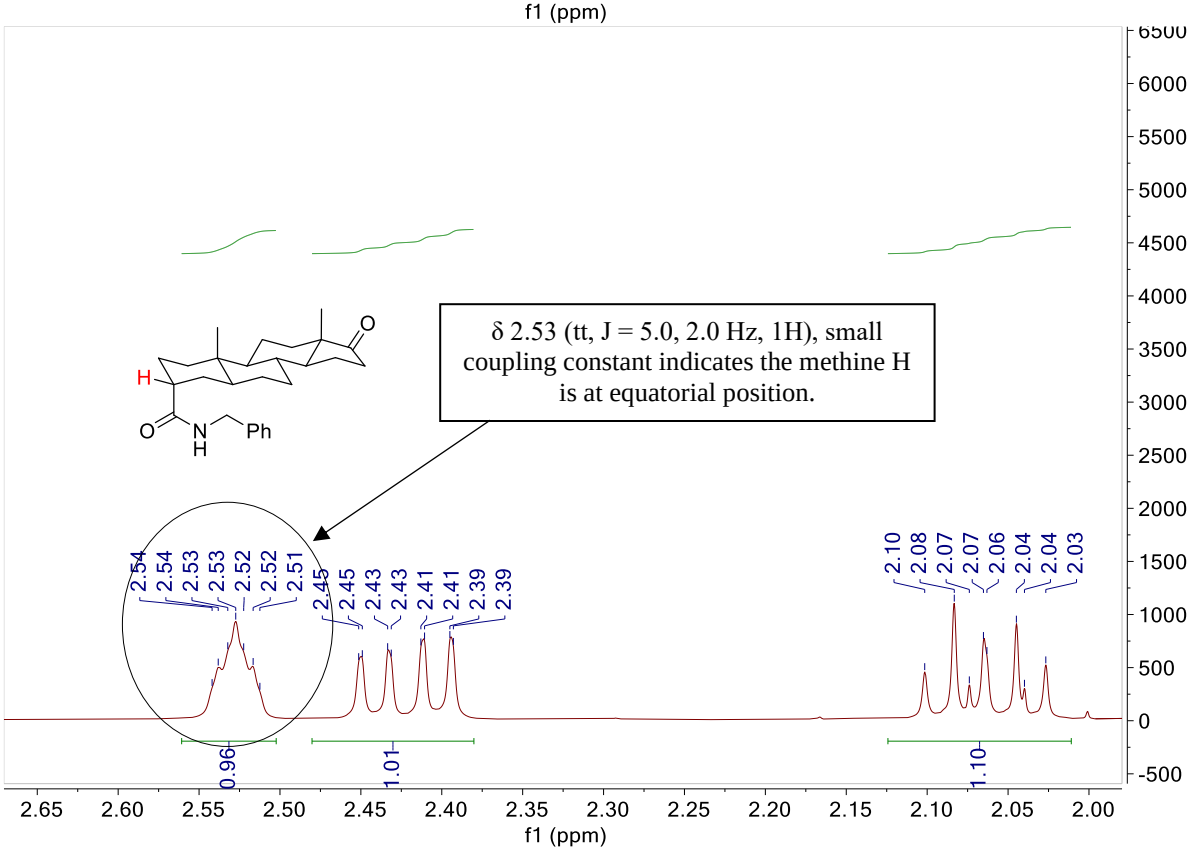
The total integration of the rest of the protons is equal to 28, which is consistent with the molecule.

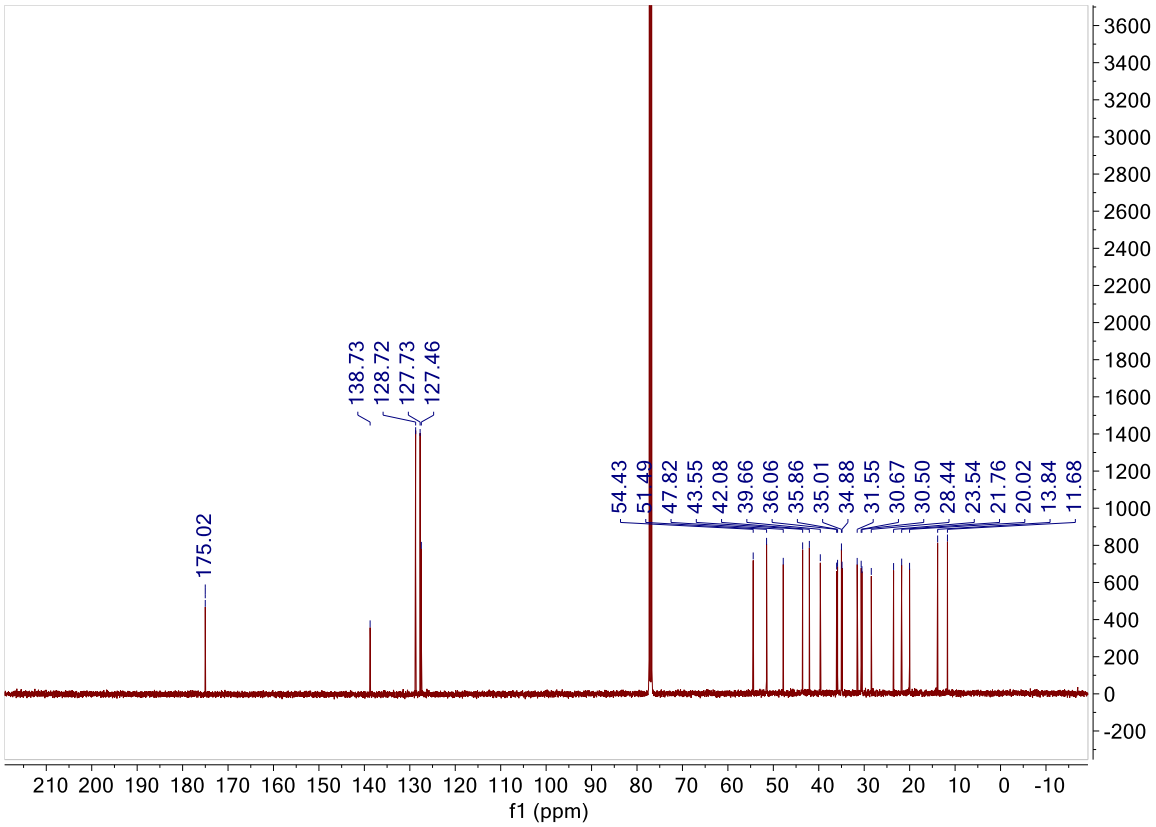

167.12
167.07
164.21
164.15
f1 (ppm)
54.33
51.16
47.44
42.82
38.81
38.46
35.96
35.26
34.75
34.62
31.51
30.45
28.56
27.98
23.43
21.98
21.35
13.16
11.40
10.97
f1 (ppm)


4f-1
4f-2
35.20
34.67
3.05
1.00
f1 (ppm)
35.20
34.67
3.05
1.00
f1 (ppm)
The ratio of the two F signals of the two diastereomers is consistent with the H ratios in the ^{1}H NMR.

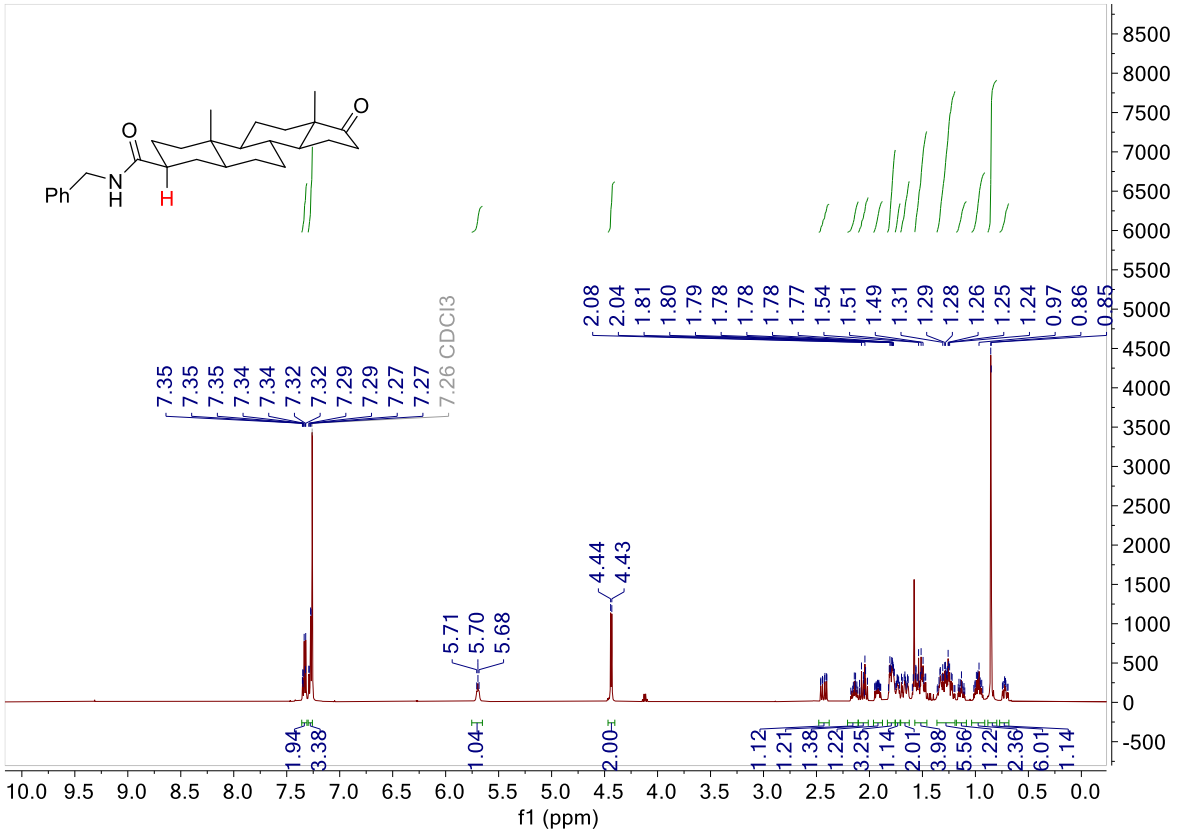
^{1}H and ^{13}C NMR data for 7f-1.

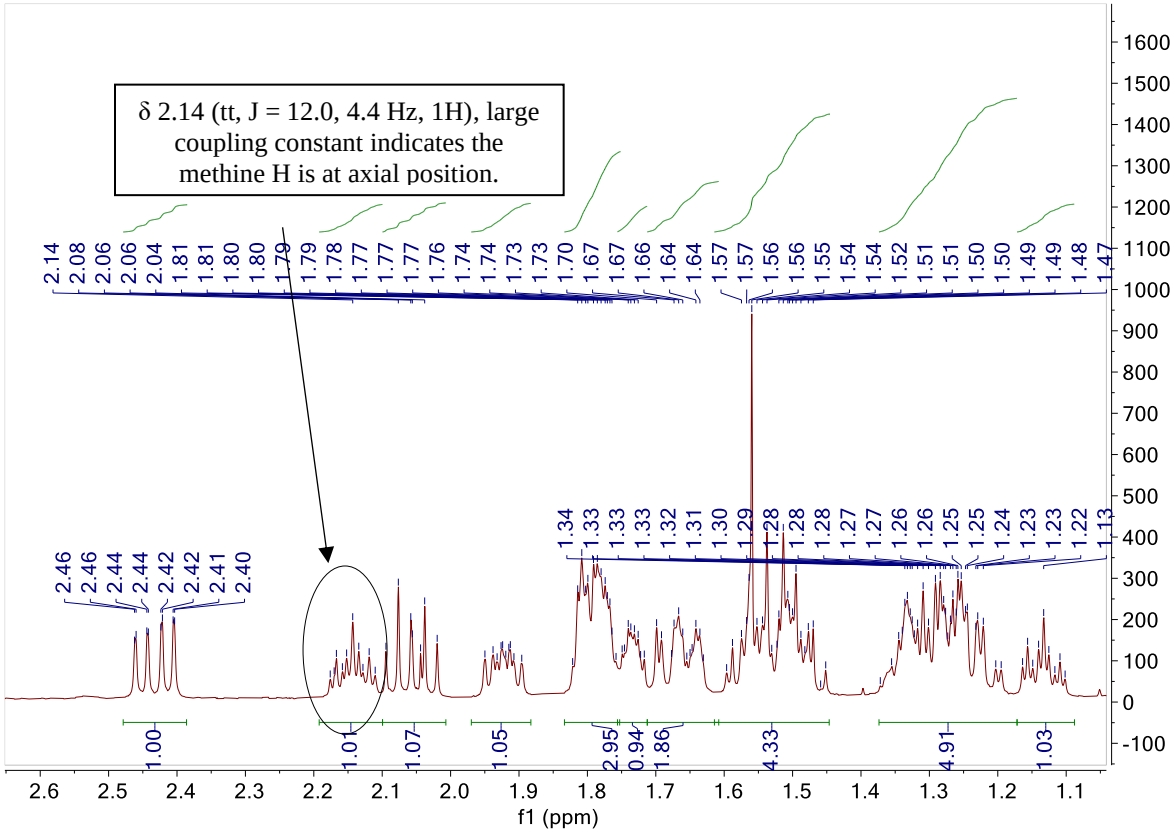


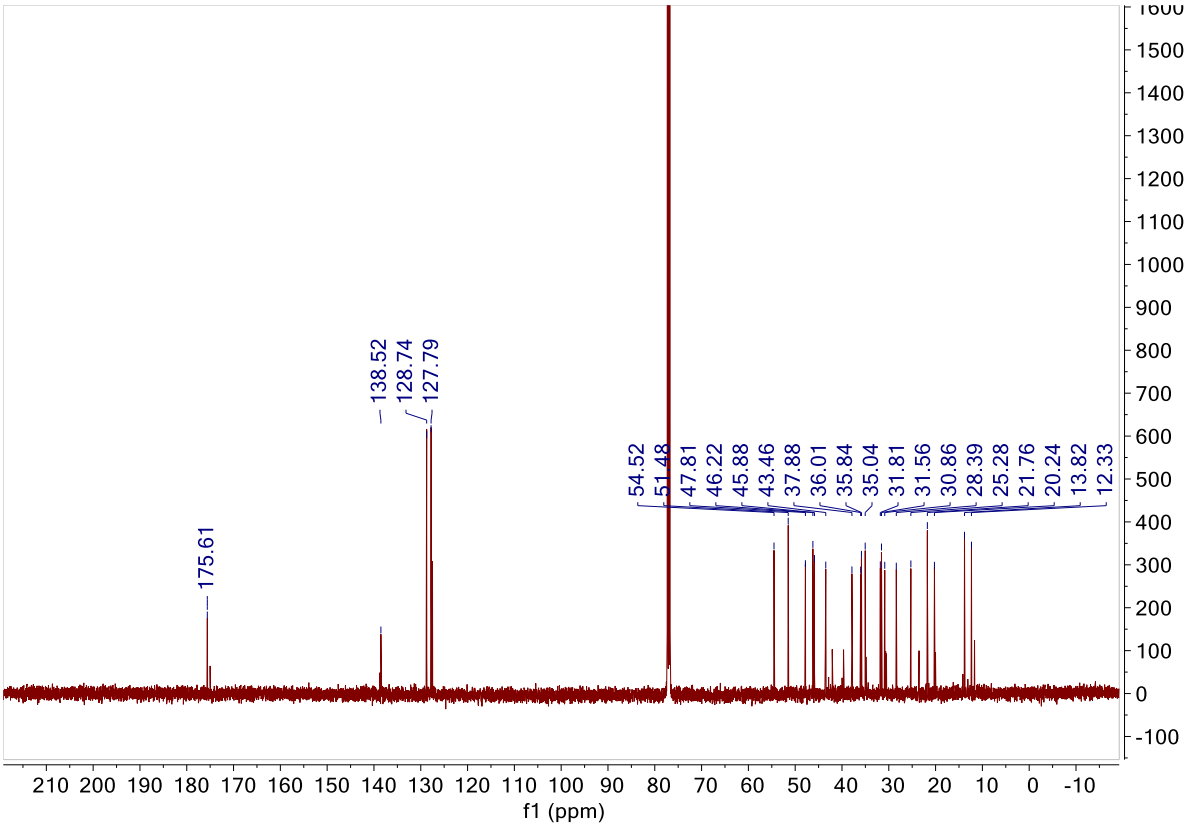



175.02
138.73
128.72
127.73
127.46
54.43
51.49
47.82
43.55
42.08
39.66
36.06
35.86
35.01
34.88
31.55
30.67
30.50
28.44
23.54
21.76
20.02
13.84
11.68
f1 (ppm)

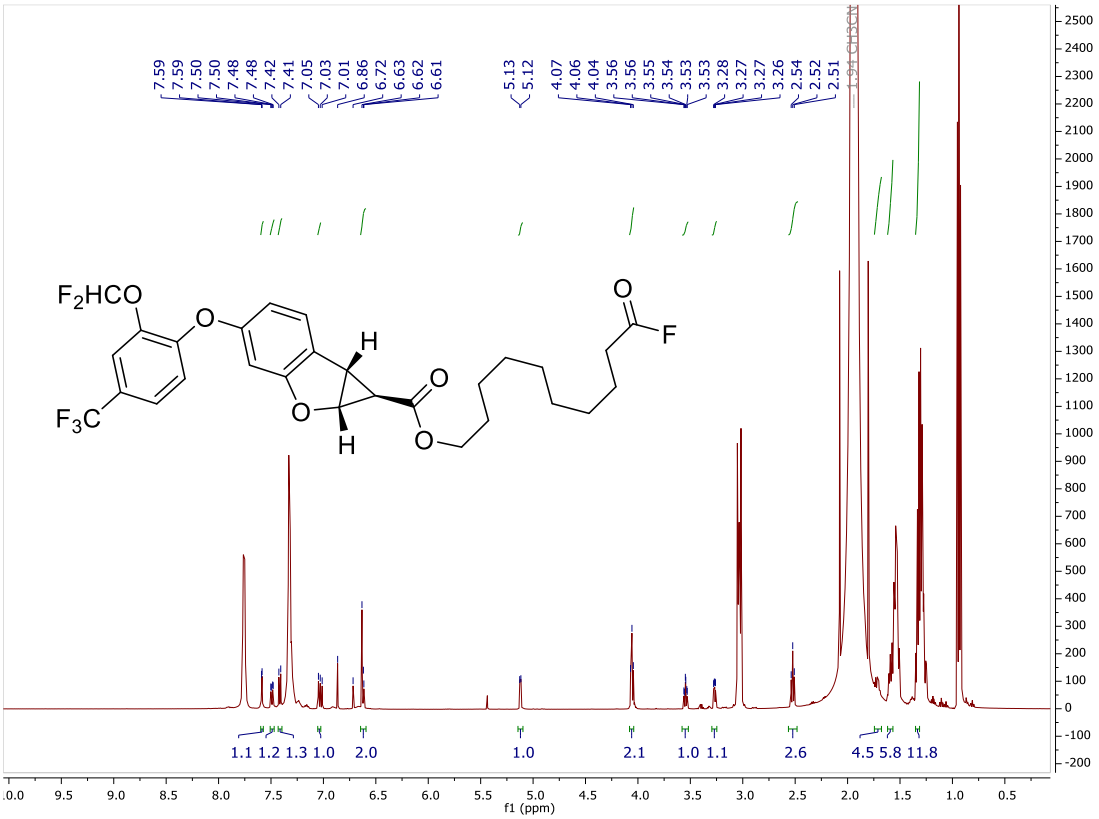
^{1}H and ^{13}C NMR data for 7f-2.

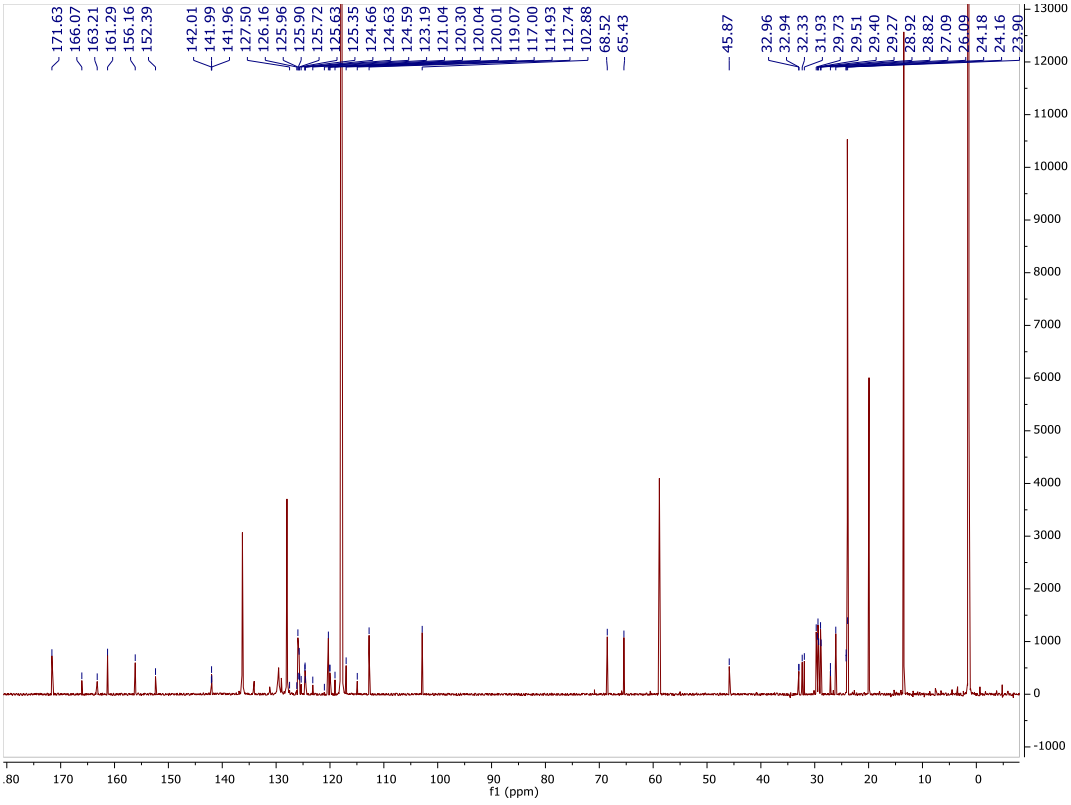


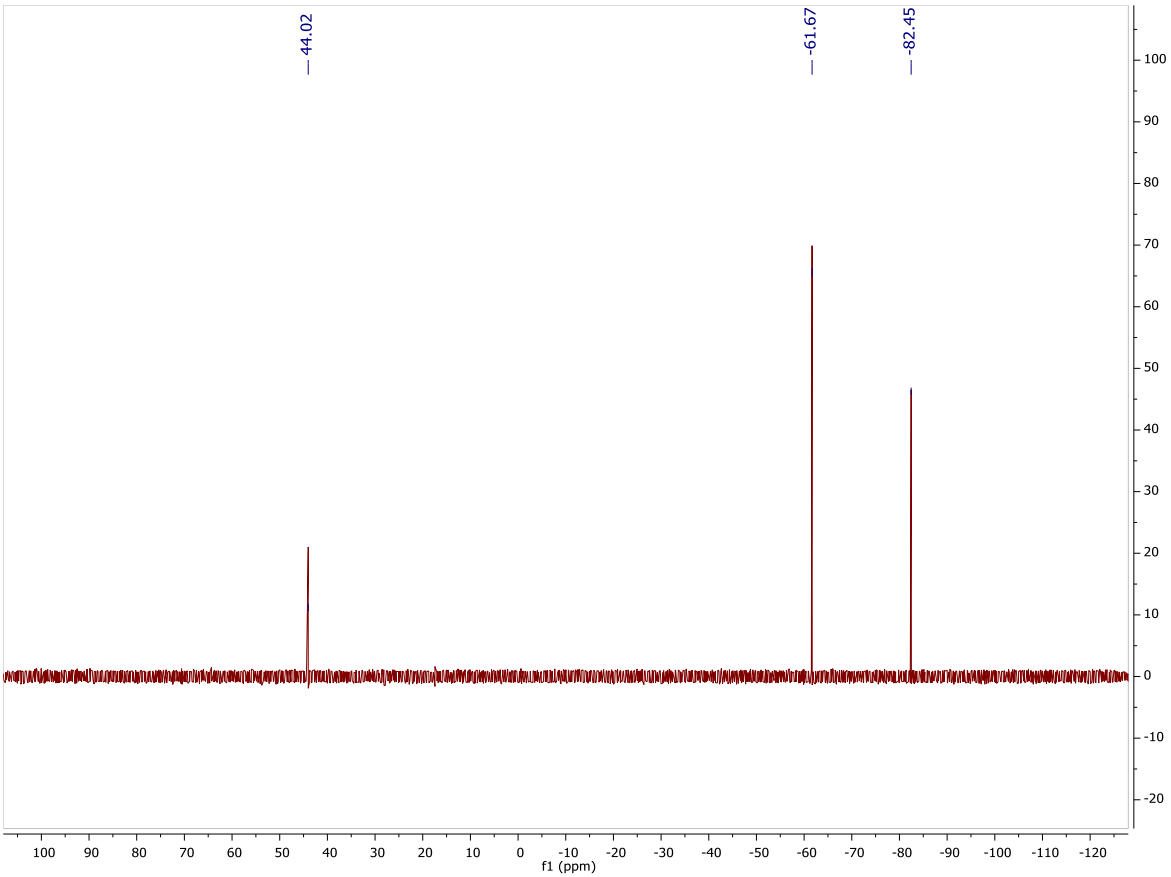



175.61
138.52
128.74
127.79
54.52
51.48
47.81
46.22
45.88
43.46
37.88
36.01
35.84
35.04
31.81
31.56
30.86
28.39
25.28
21.76
20.24
13.82
12.33
f1 (ppm)

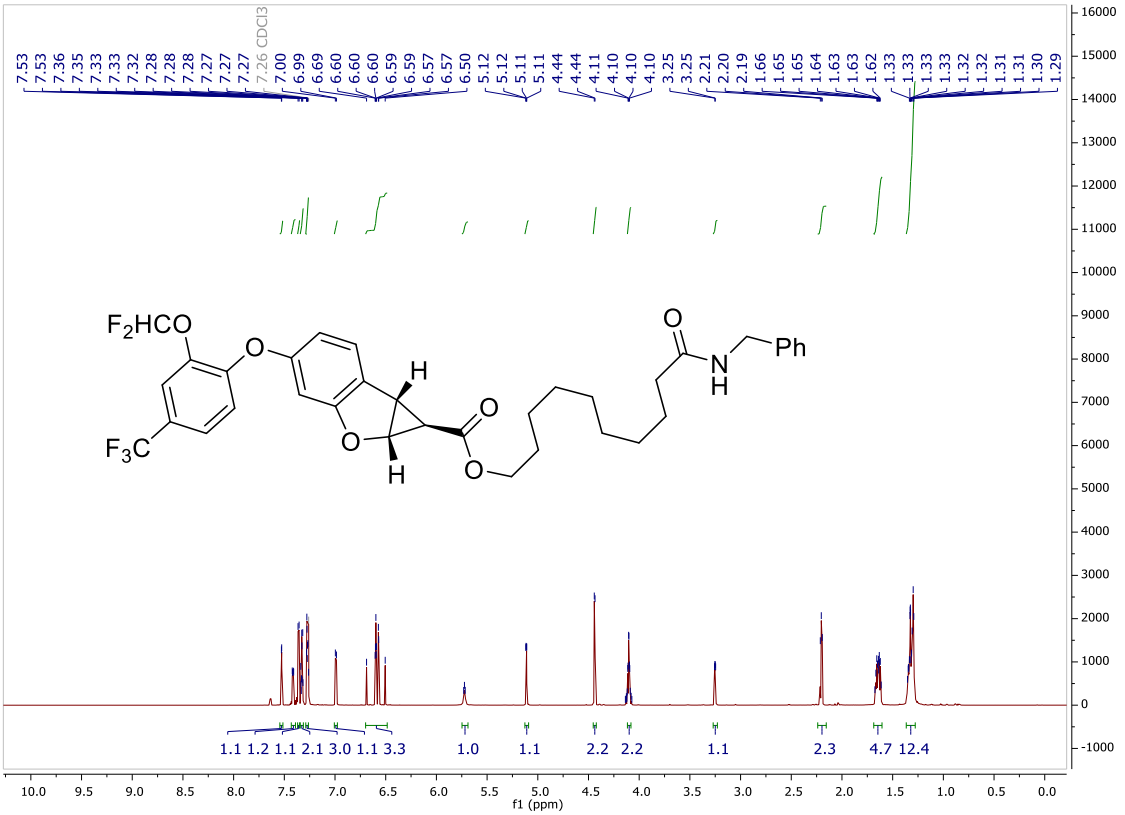
In situ ^{1}H, ^{13}C, and ^{19}F NMR data for 4g

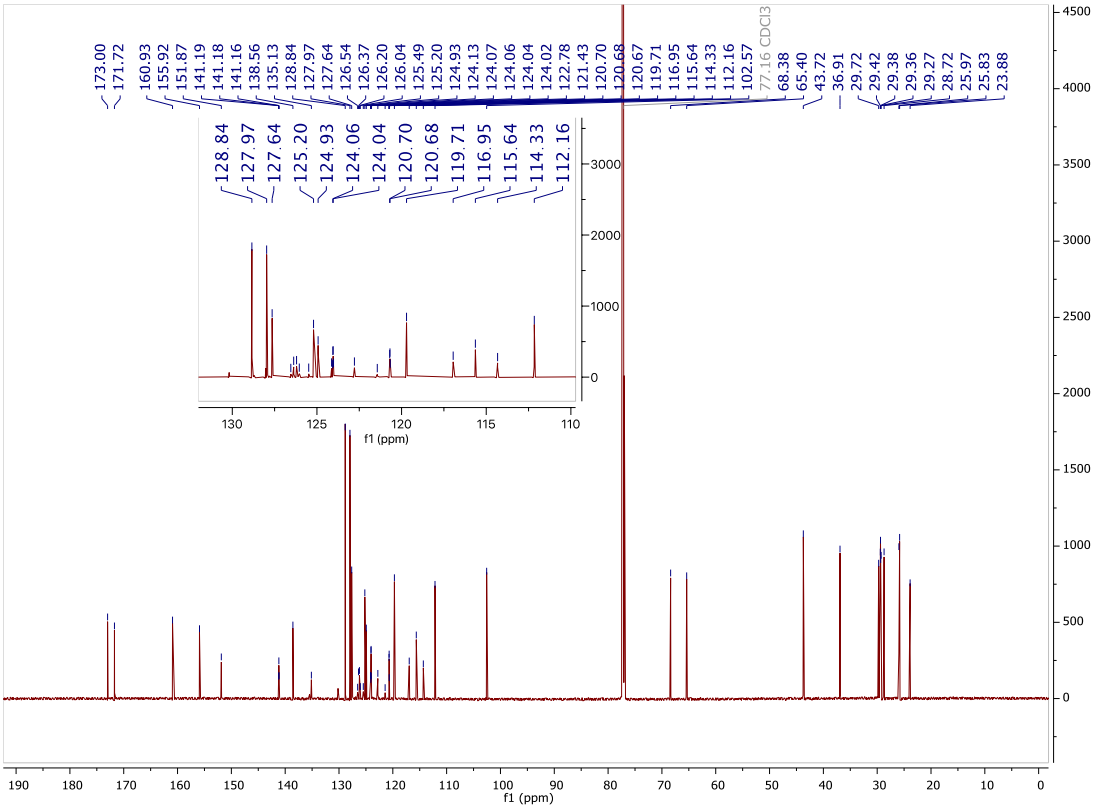


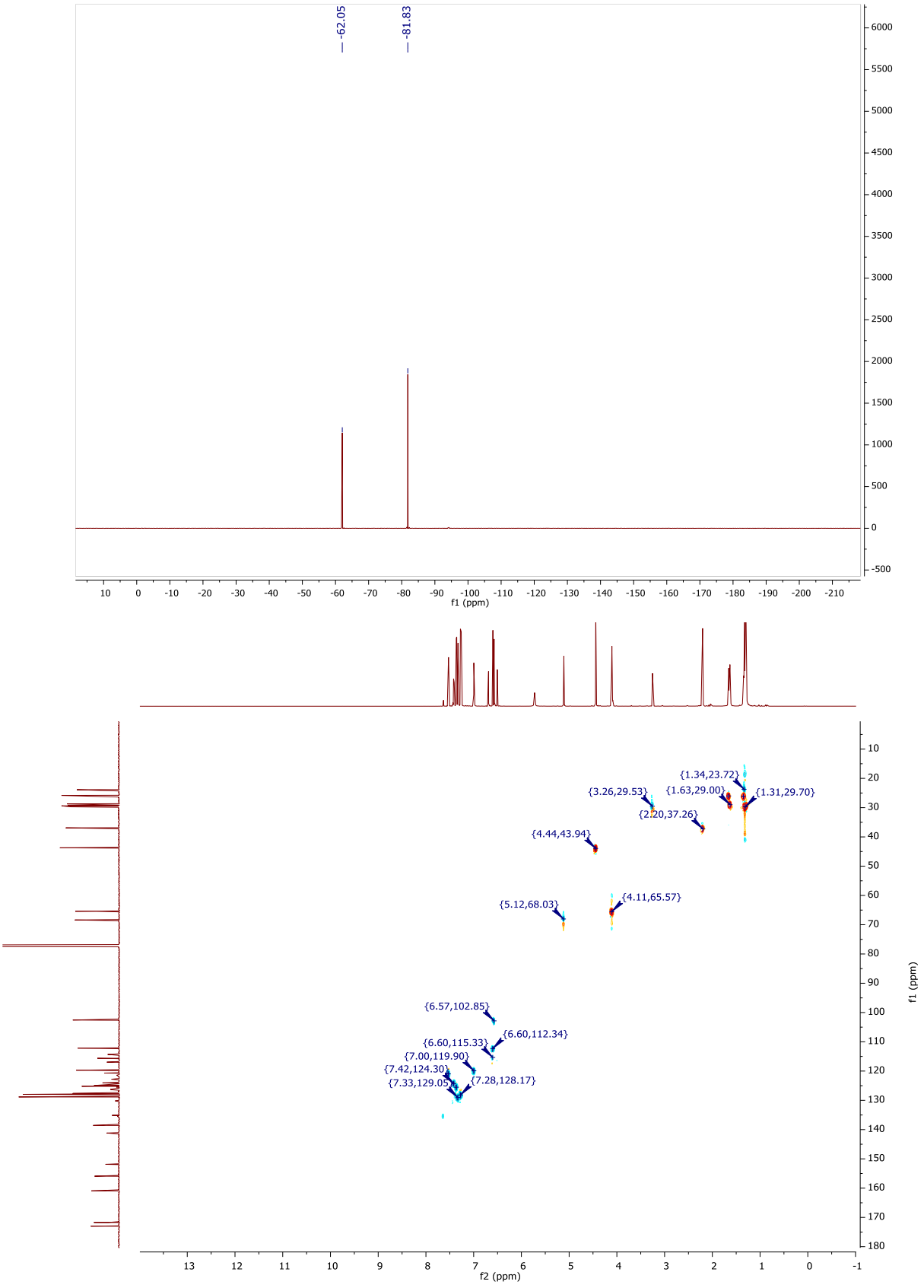



44.02
-61.67
-82.45
100
90
80
70
60
50
40
30
20
10
0
-10
-20
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120
f1 (ppm)

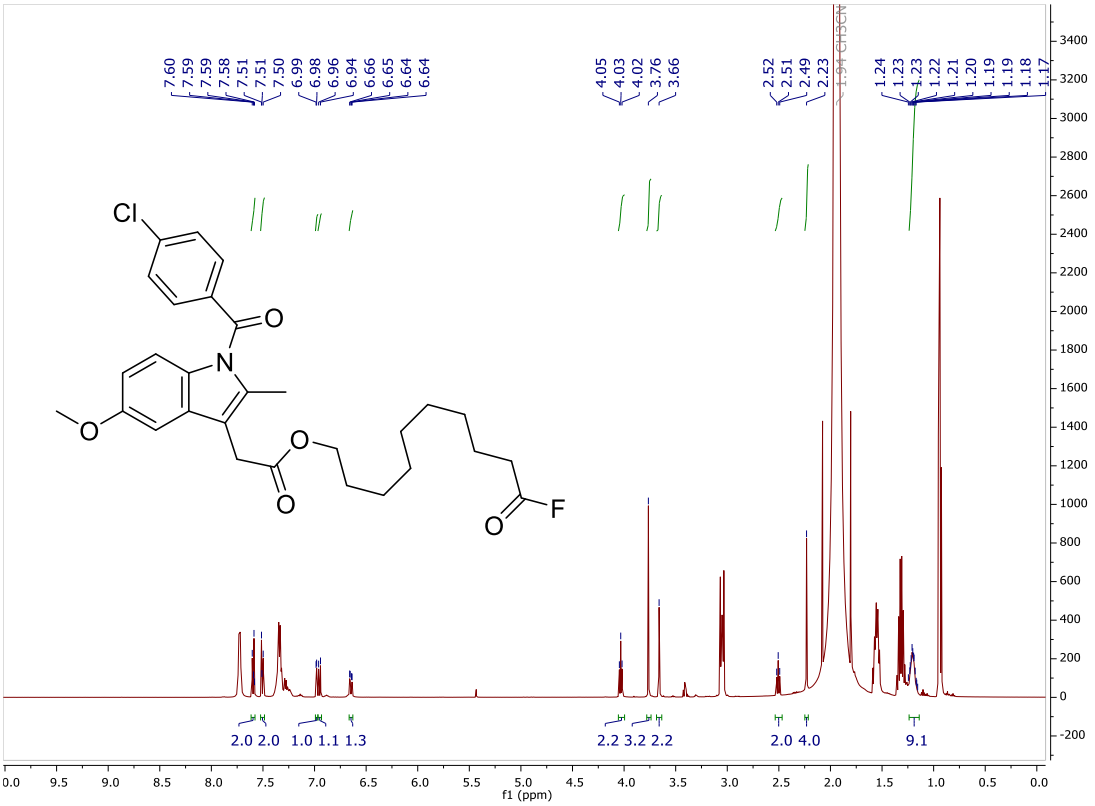
^{1}H, ^{13}C, ^{19}F and HSQC NMR data for 7g

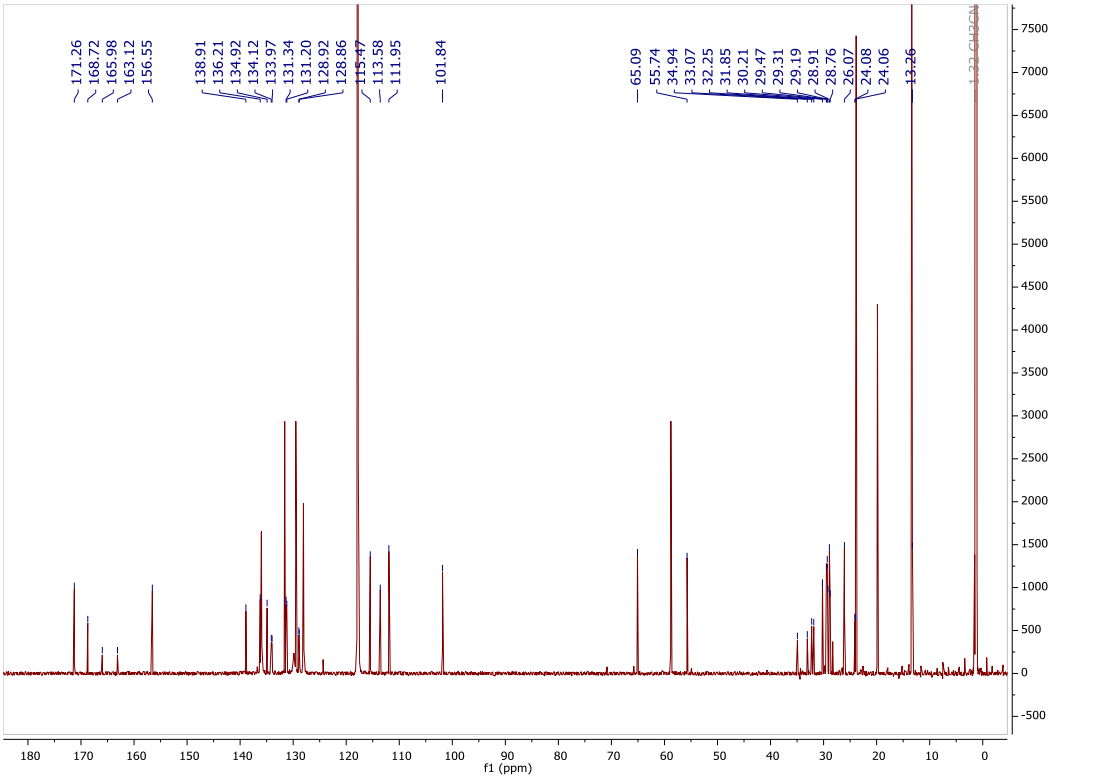


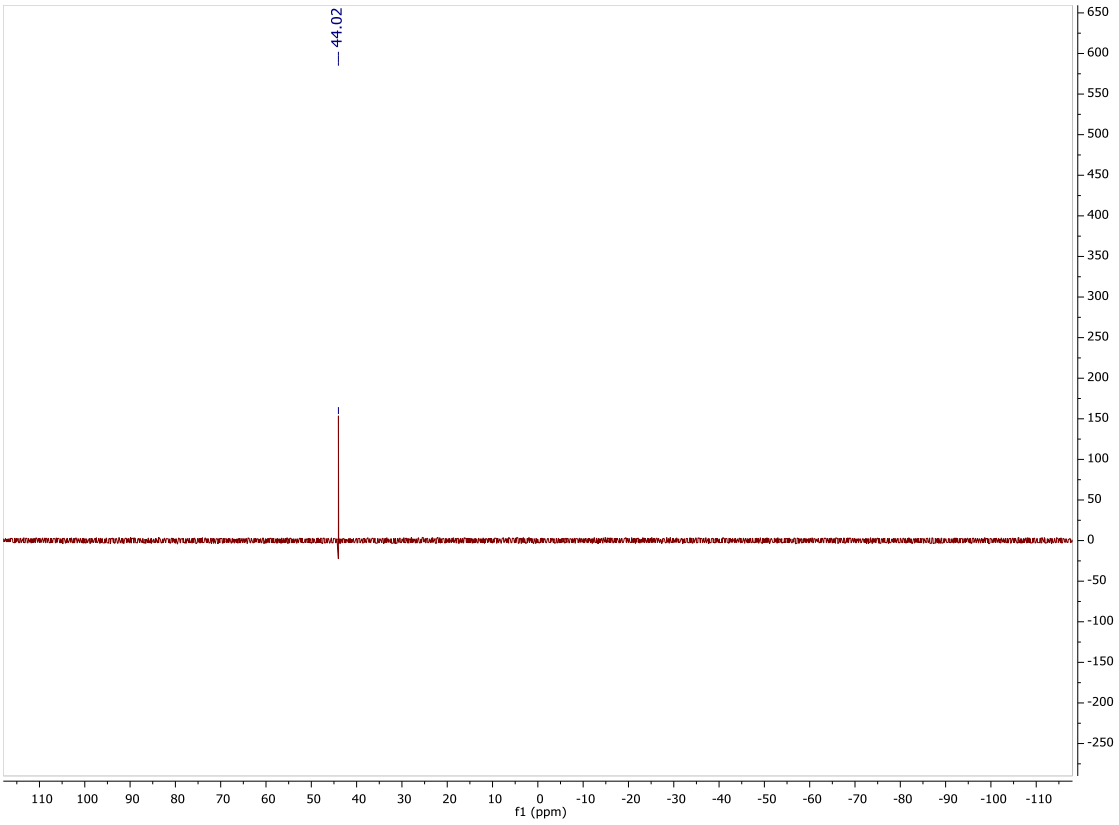



-62.05
-81.83
f1 (ppm)
{1.34,23.72}
{1.63,29.00}
{1.31,29.70}
{3.26,29.53}
{2.20,37.26}
{4.44,43.94}
{4.11,65.57}
{5.12,68.03}
{6.57,102.85}
{6.60,112.34}
{6.60,115.33}
{7.00,119.90}
{7.42,124.30}
{7.33,129.05}
{7.28,128.17}
f2 (ppm)
f1 (ppm)

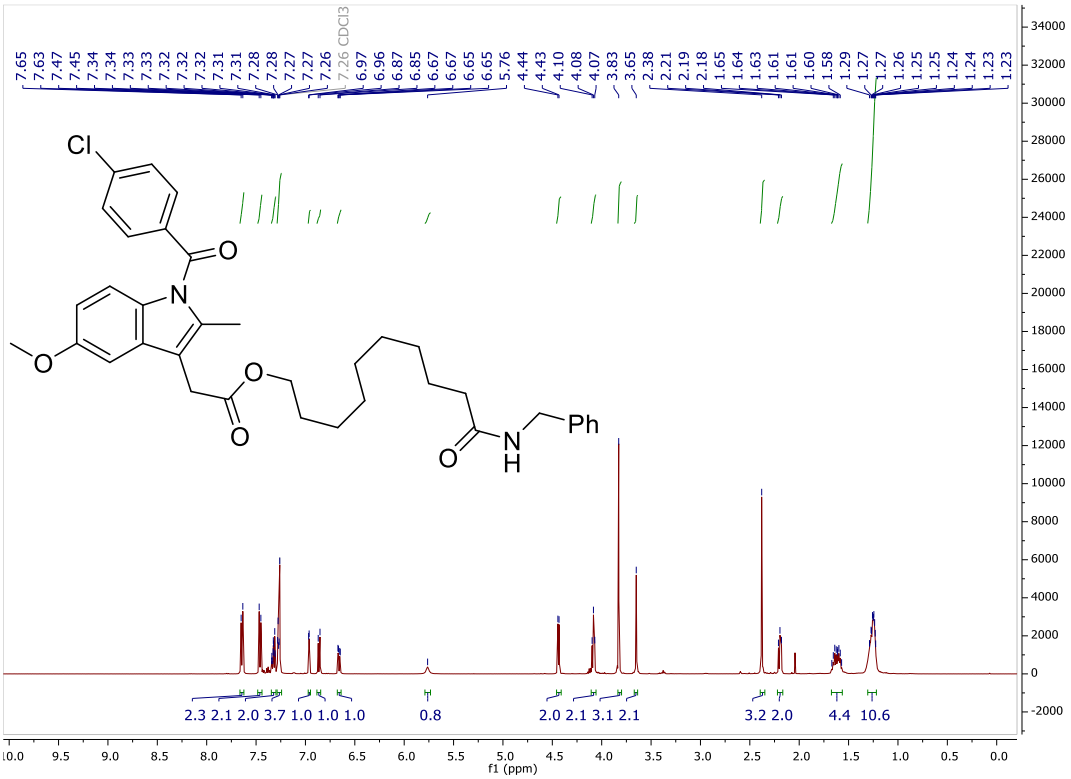
In situ ^{1}H, ^{13}C, and ^{19}F NMR data for 4h

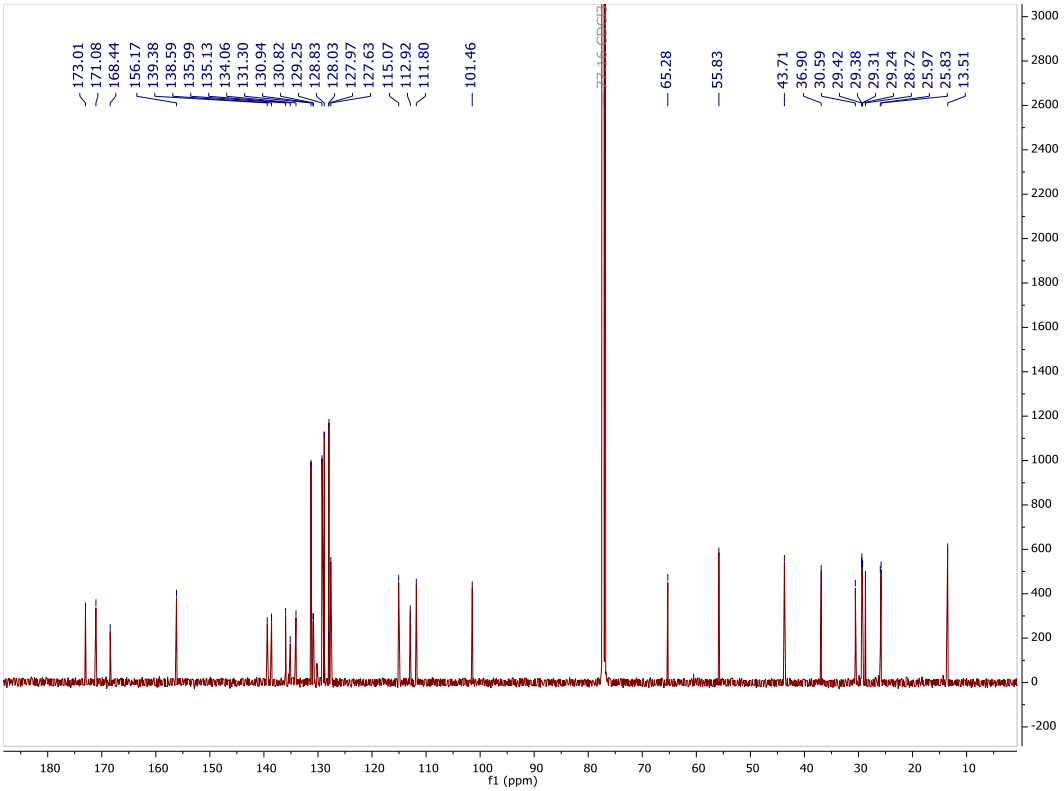




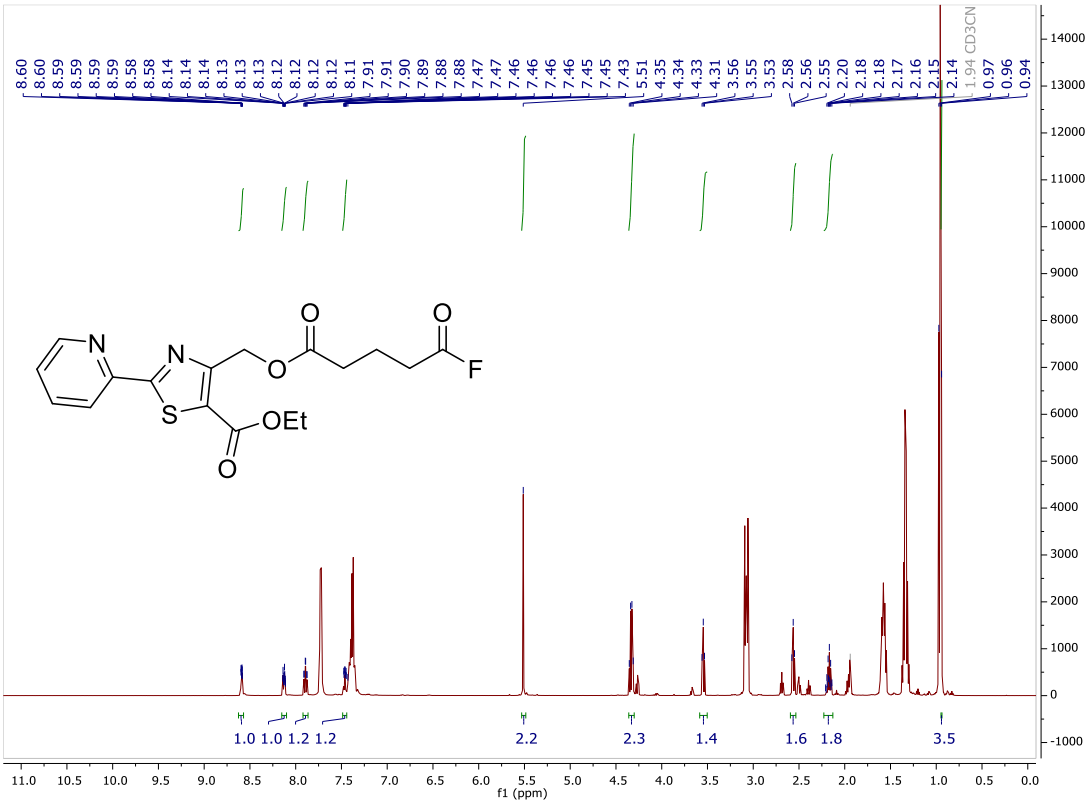

44.02
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110
f1 (ppm)

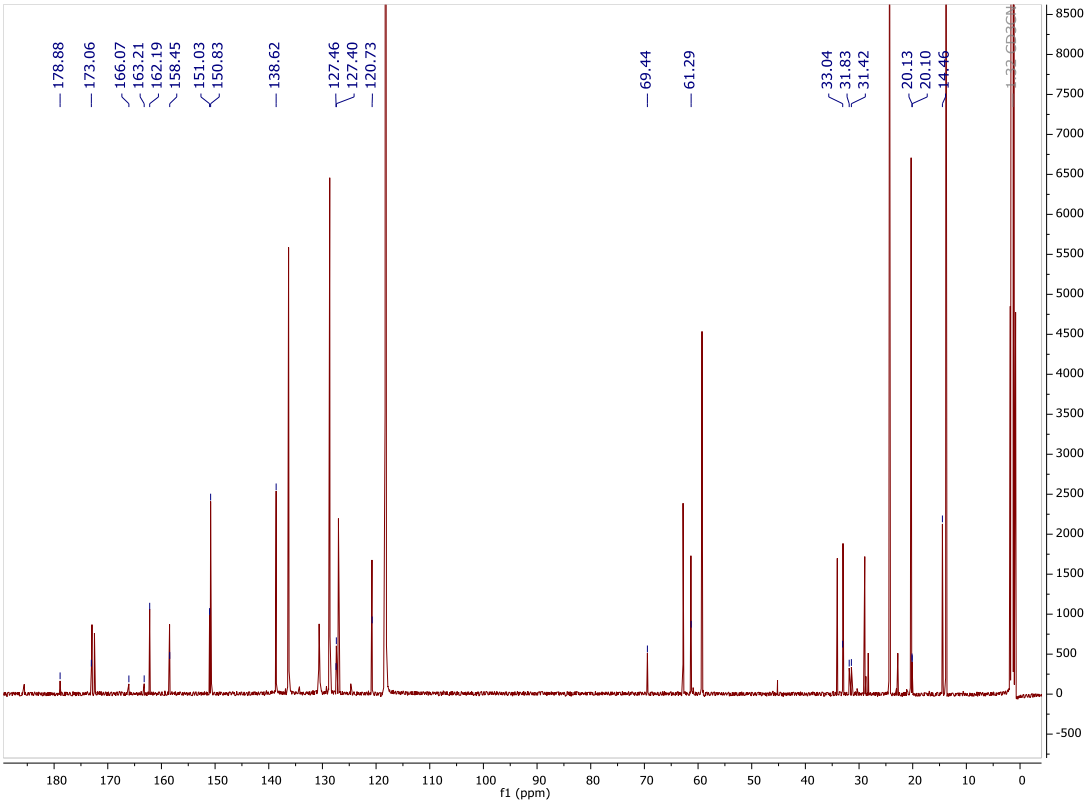
^{1}H and ^{13}C NMR data for 7h.

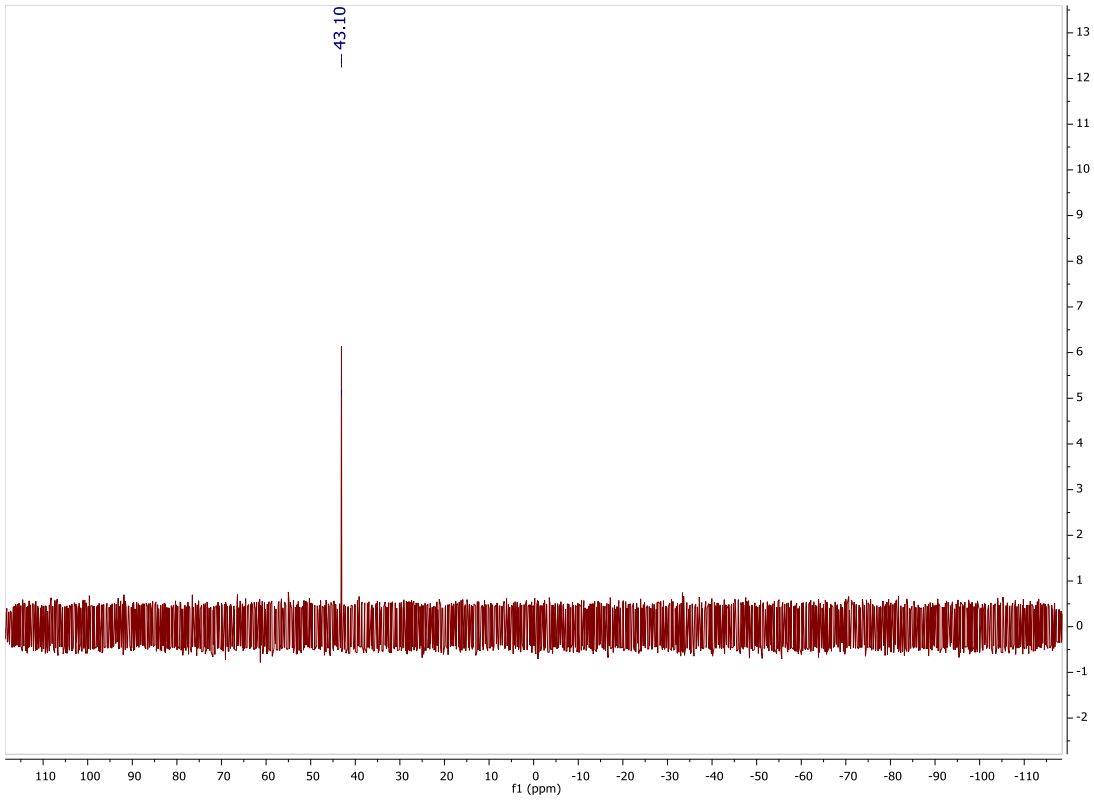




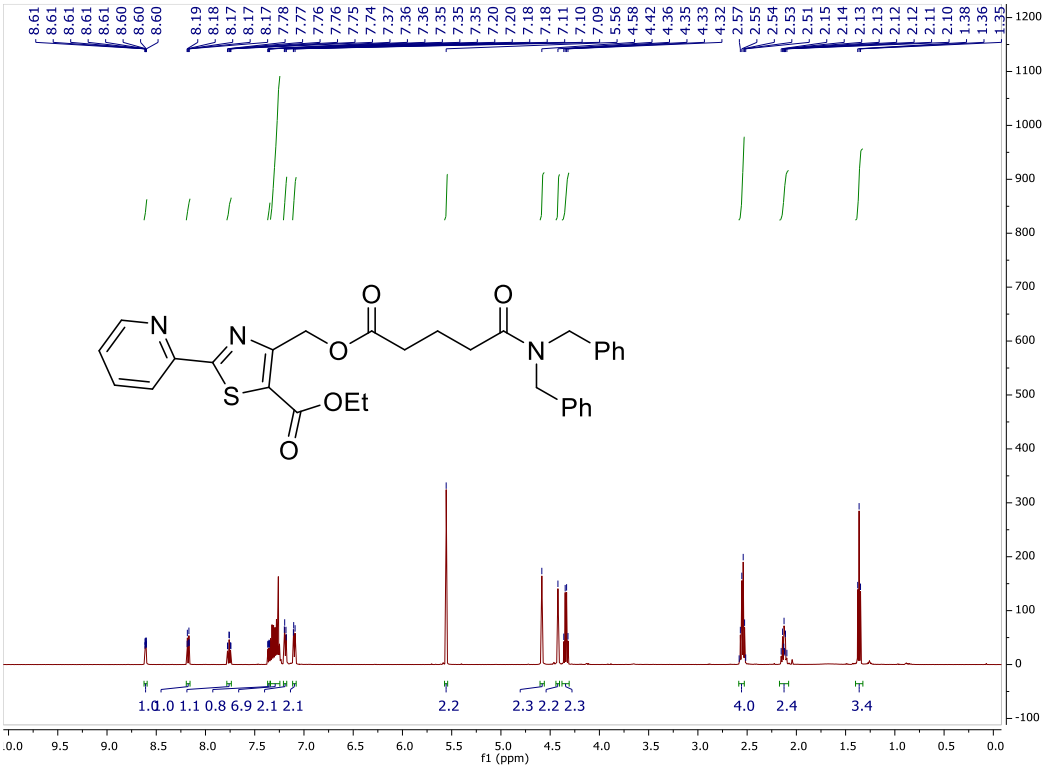
***In situ* ^{1}H, ^{13}C, and ^{19}F NMR data for 4i.**

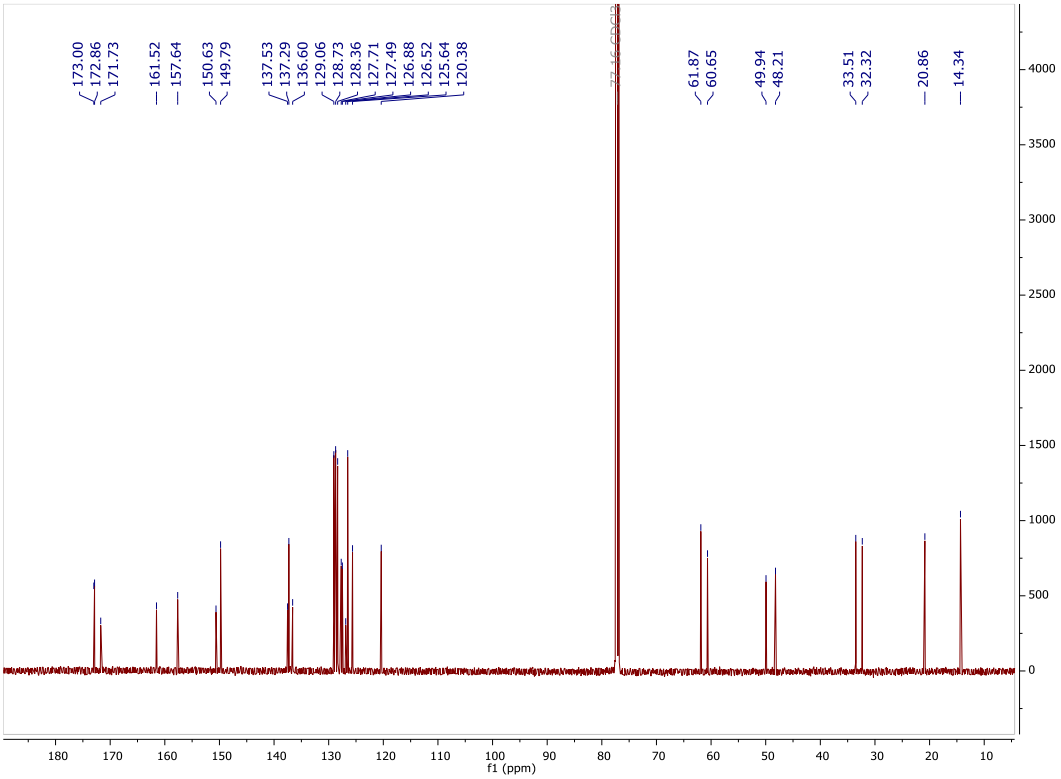




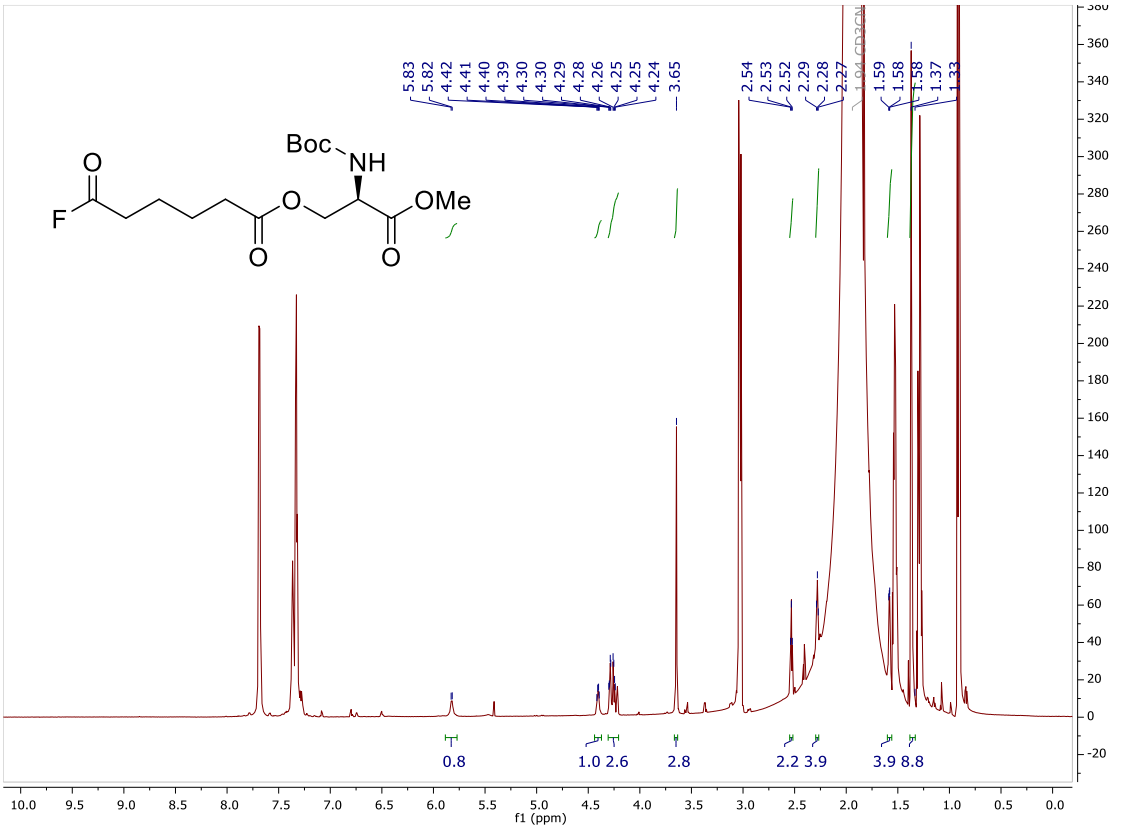

43.10
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
f1 (ppm)

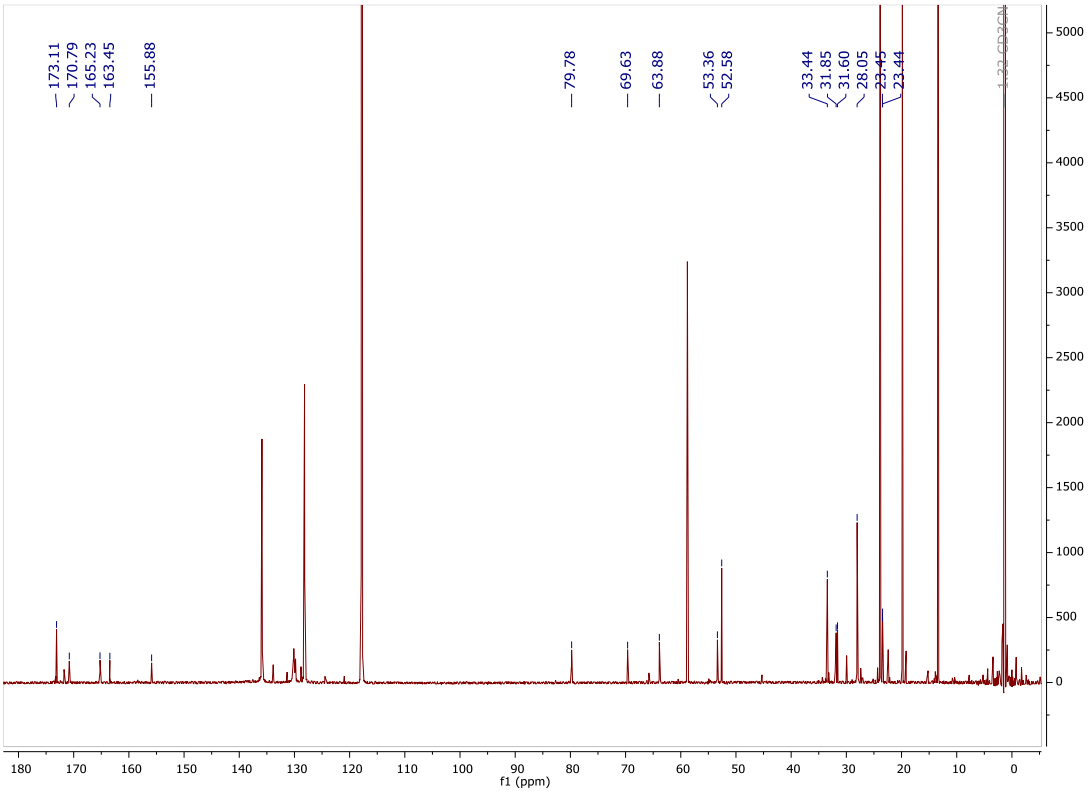
^{1}H and ^{13}C NMR data for 7i

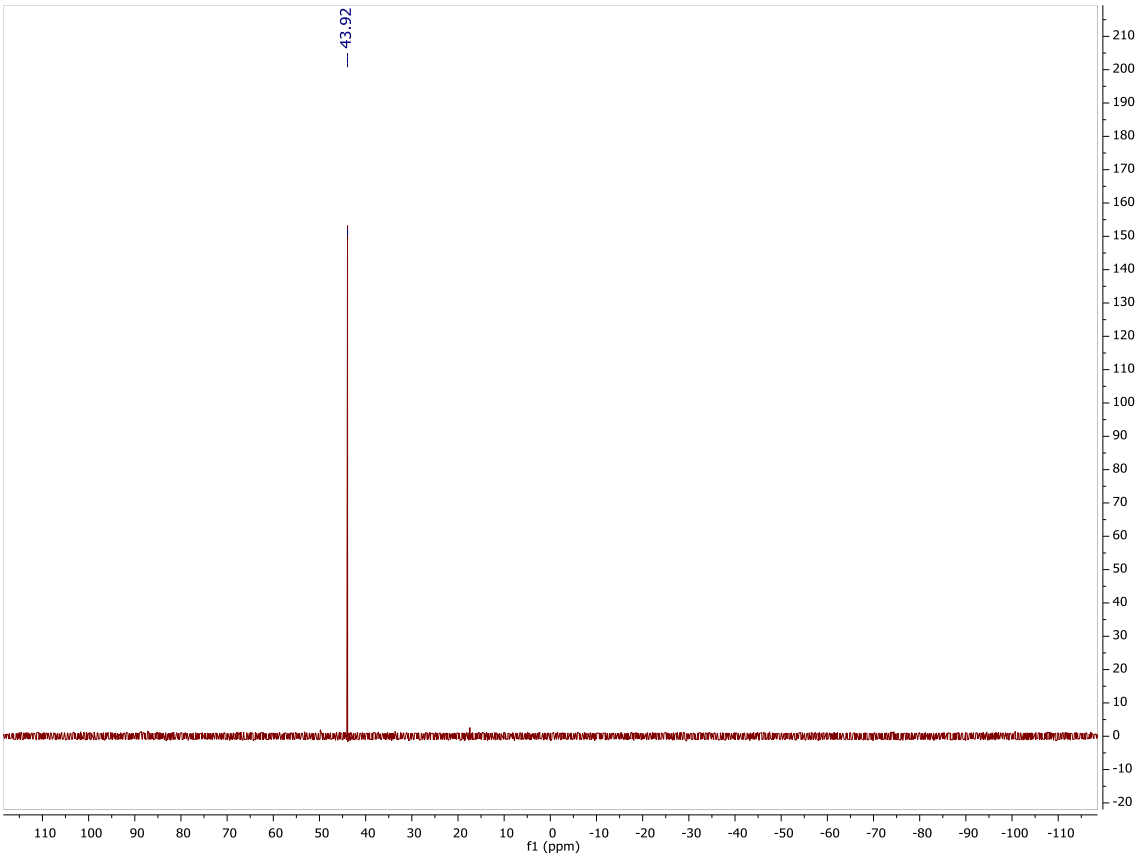




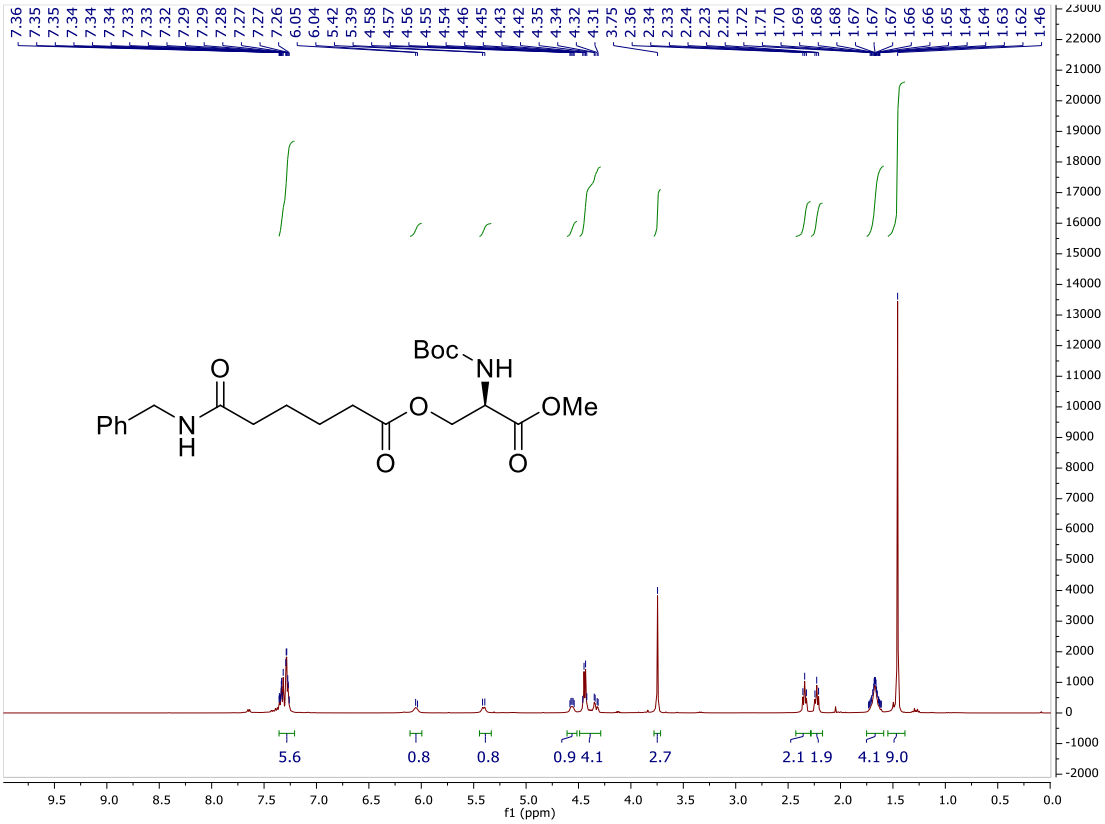
In situ ^{1}H, ^{13}C, and ^{19}F NMR data for 4j

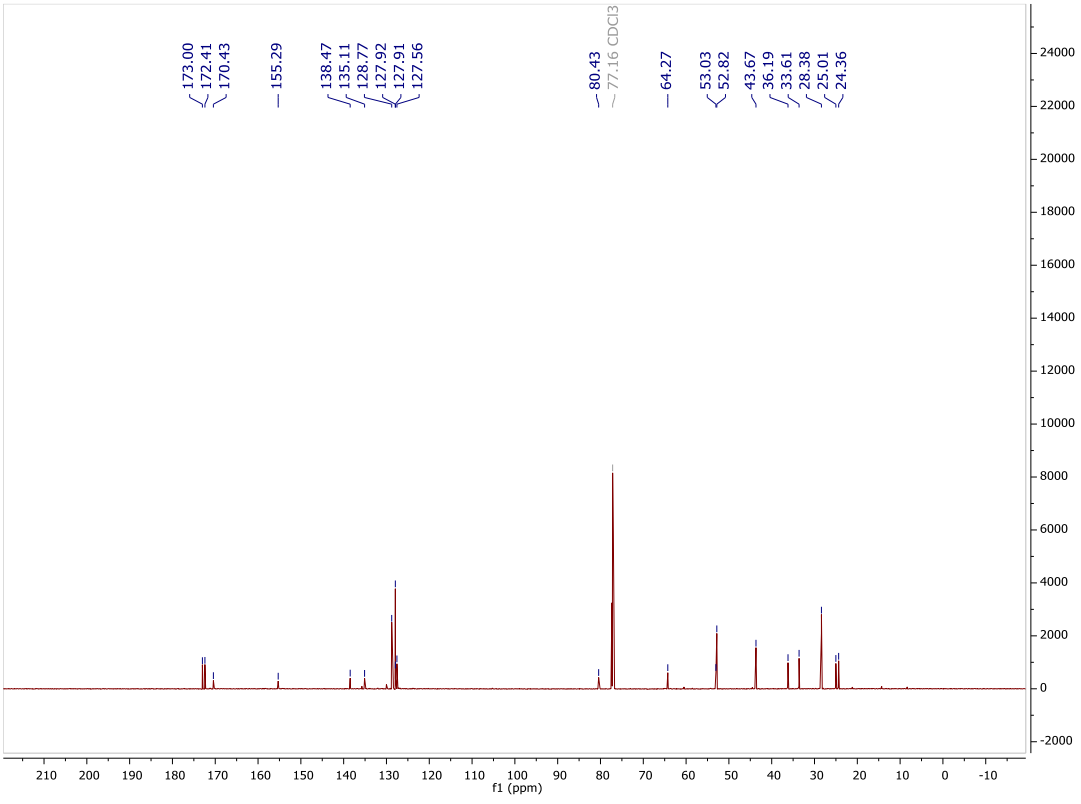




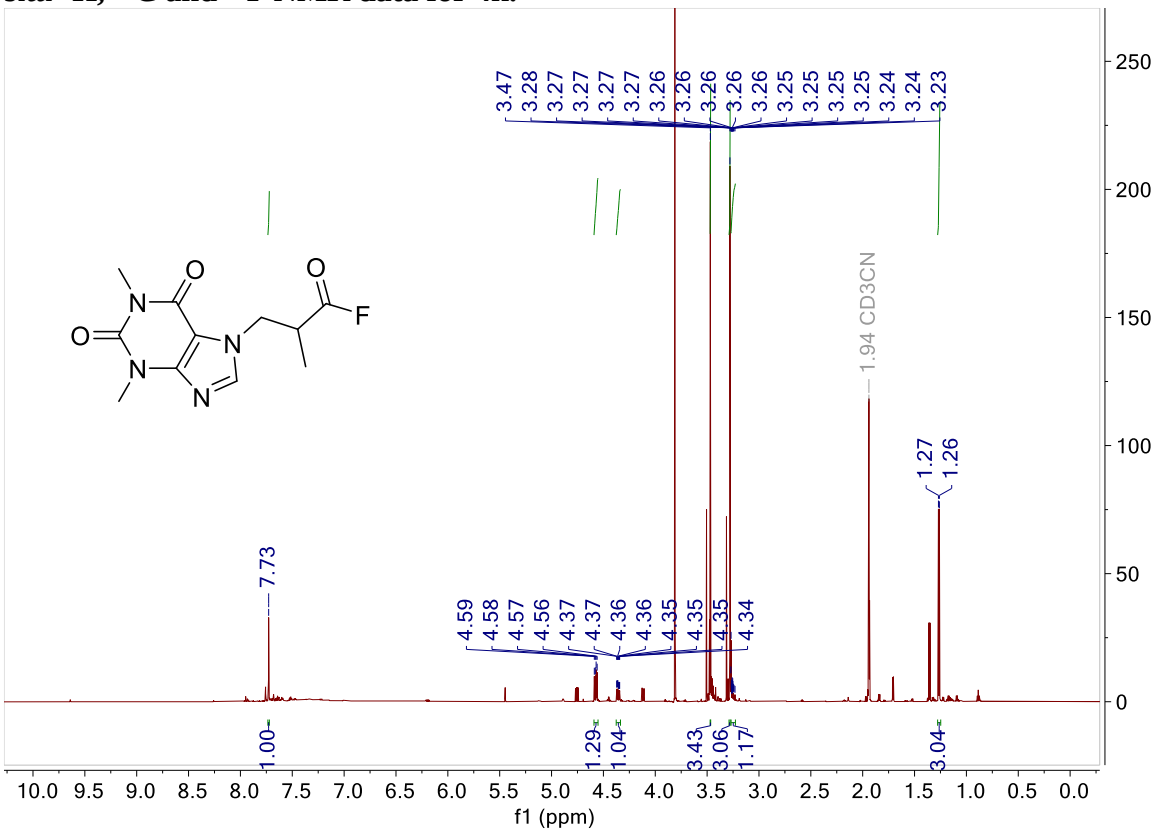

43.92
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110
f1 (ppm)

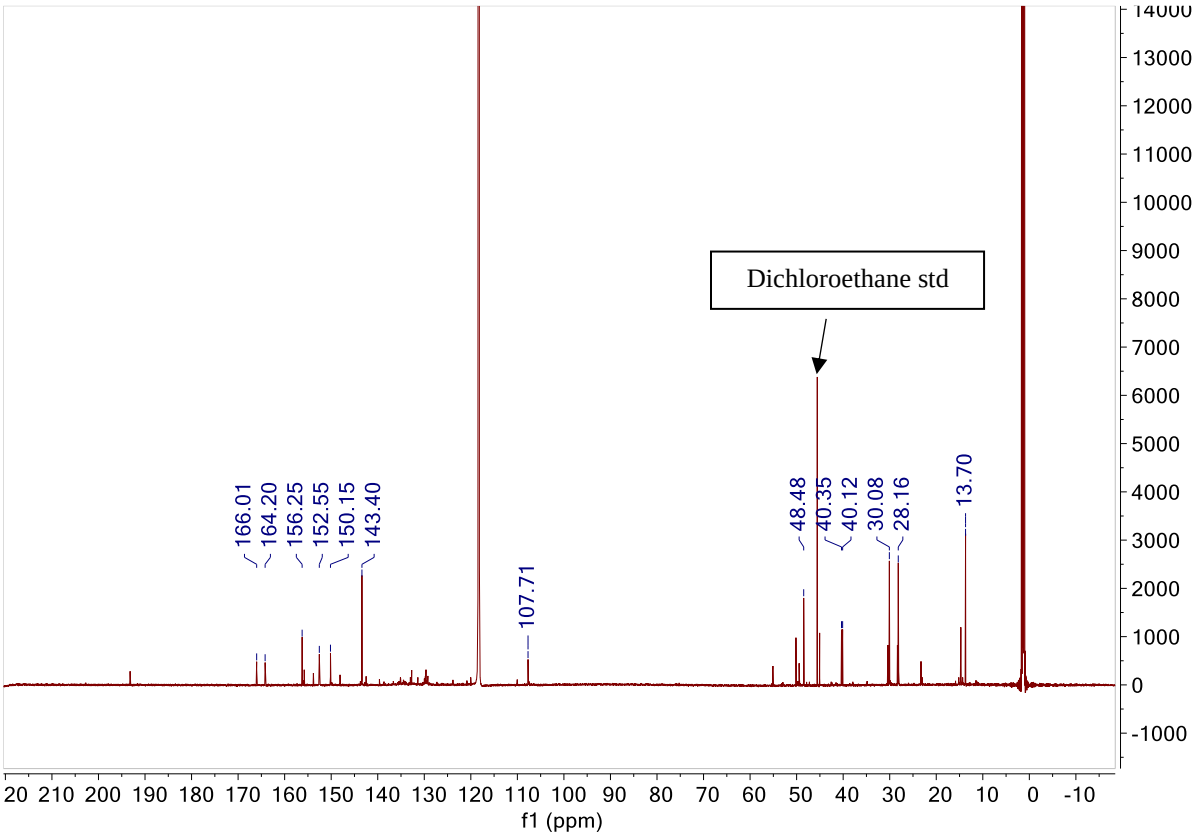
^{1}H and ^{13}C NMR data for 7j

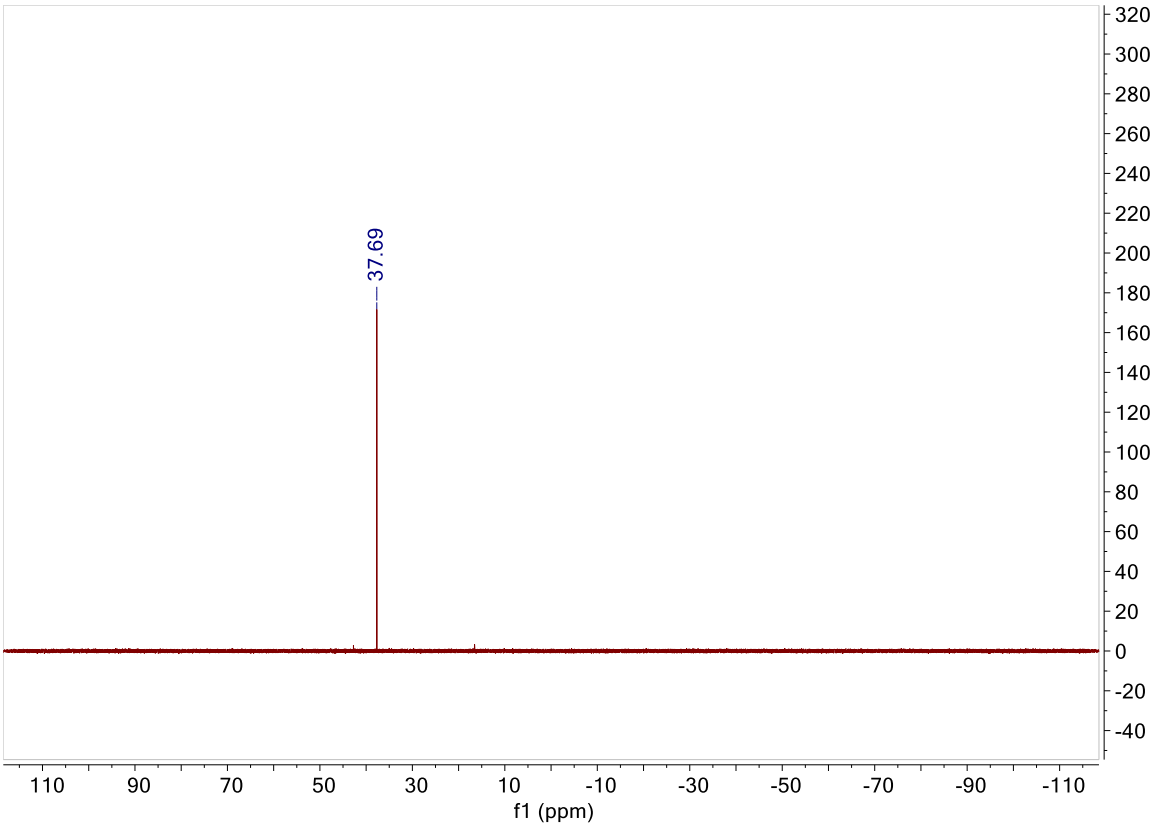




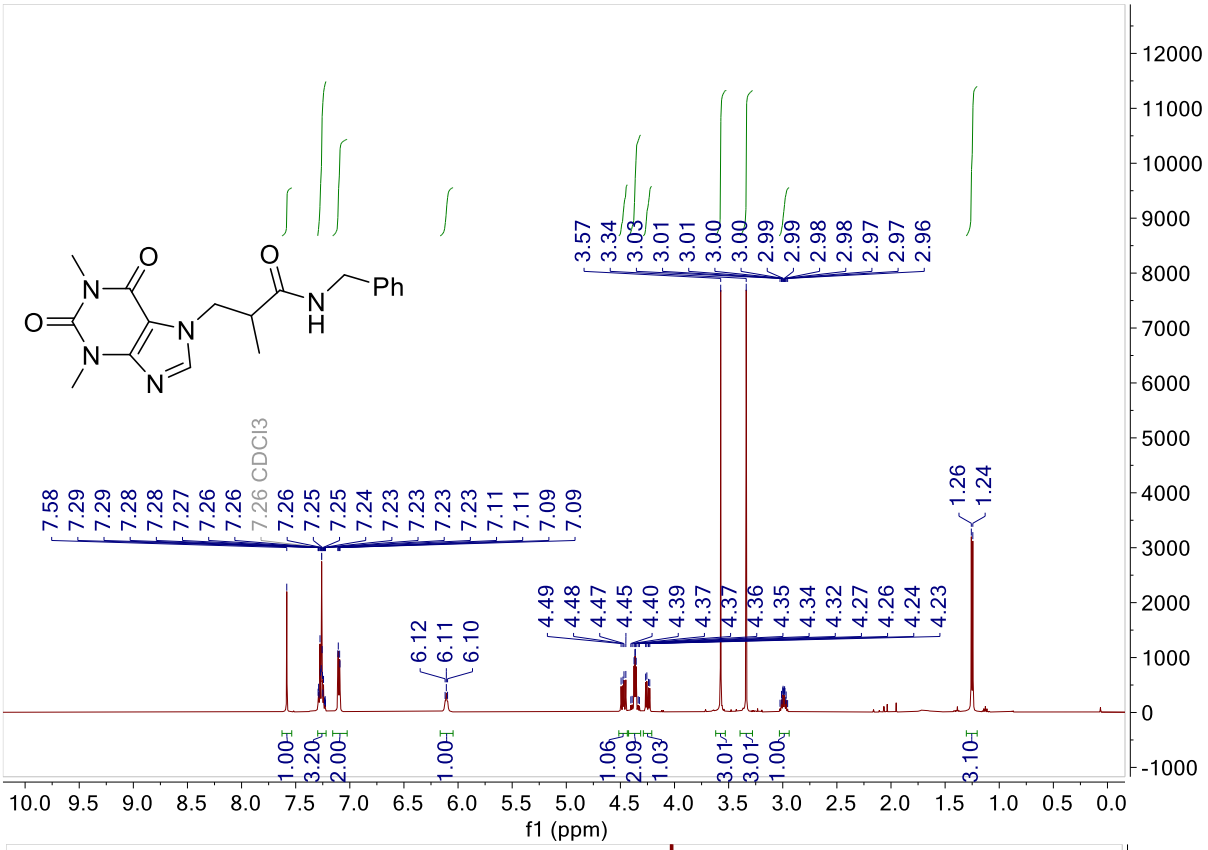
***In situ* ^{1}H, ^{13}C and ^{19}F NMR data for 4k.**

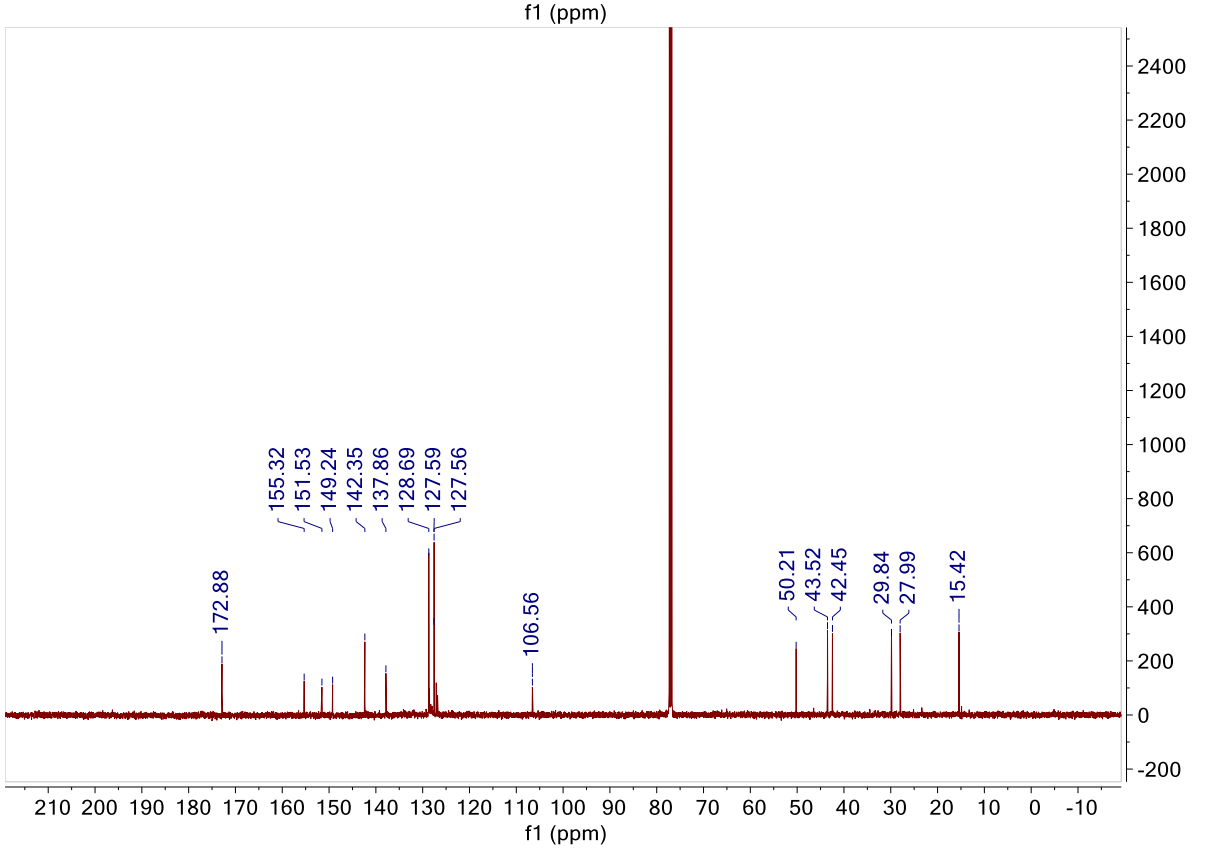




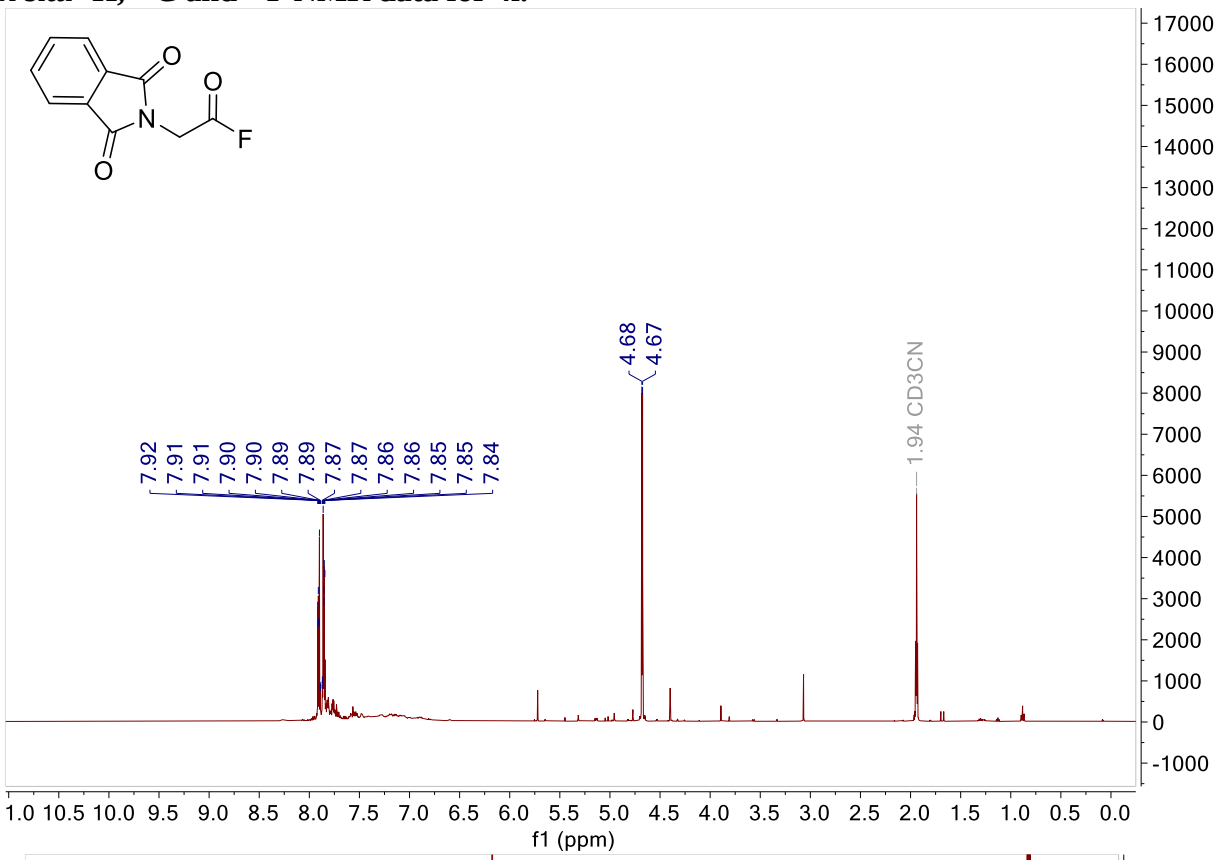

37.69
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
110
90
70
50
30
10
-10
-30
-50
-70
-90
-110
f1 (ppm)

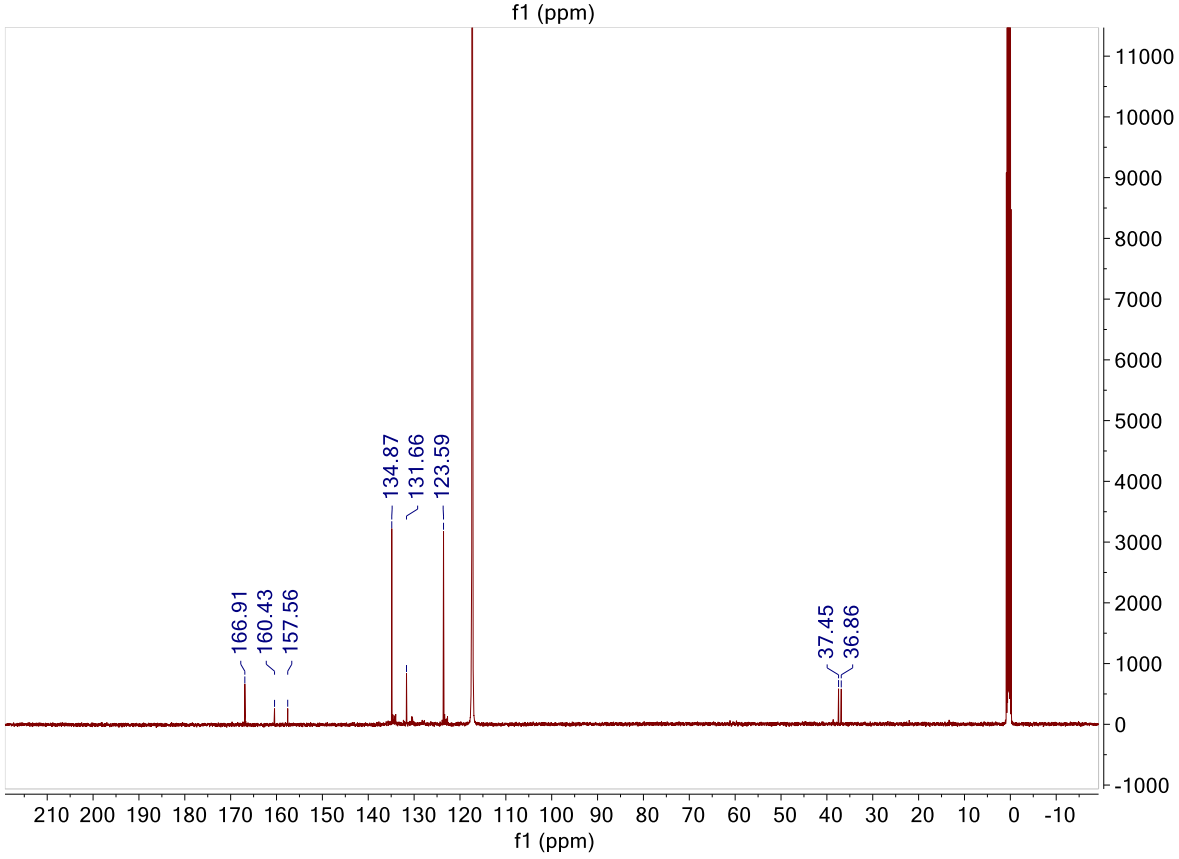
^{1}H and ^{13}C NMR data for 7k.

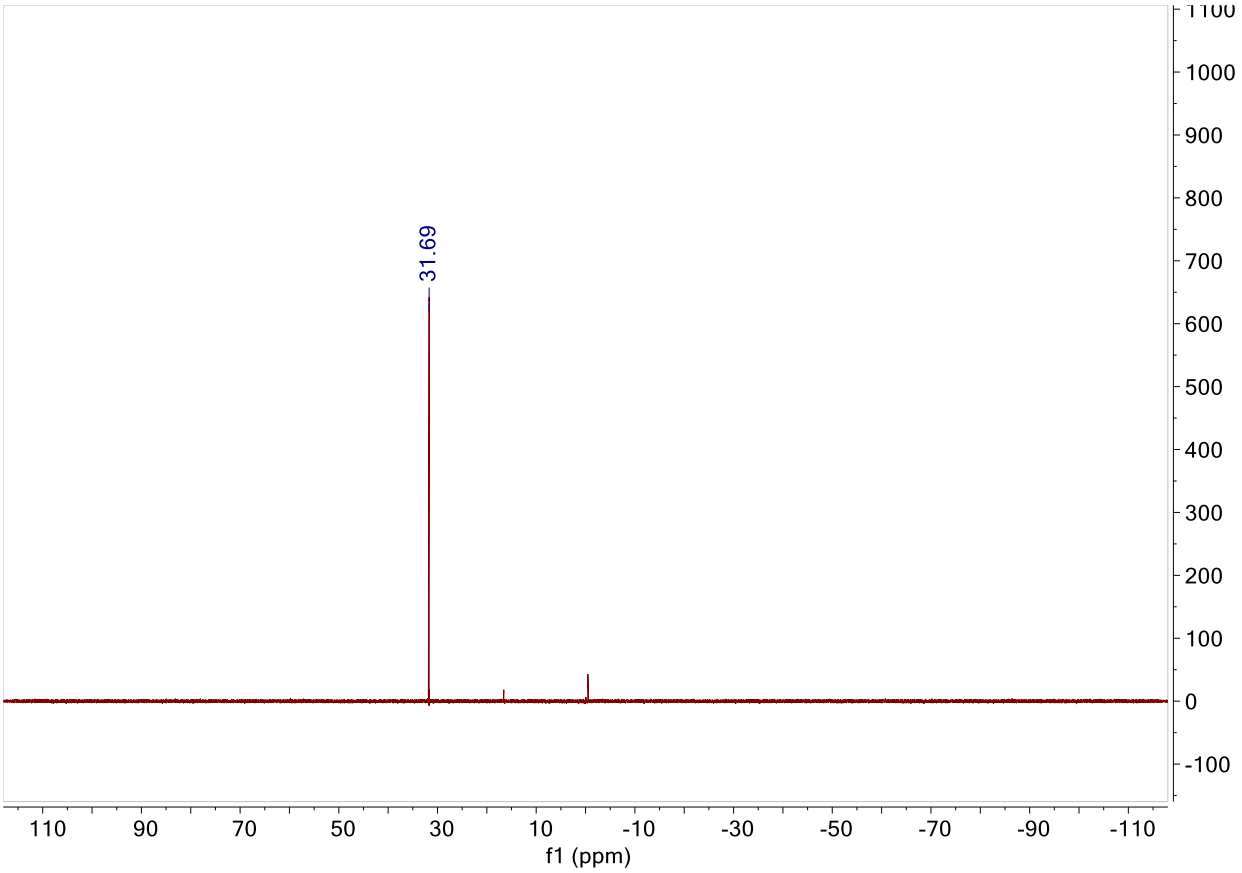




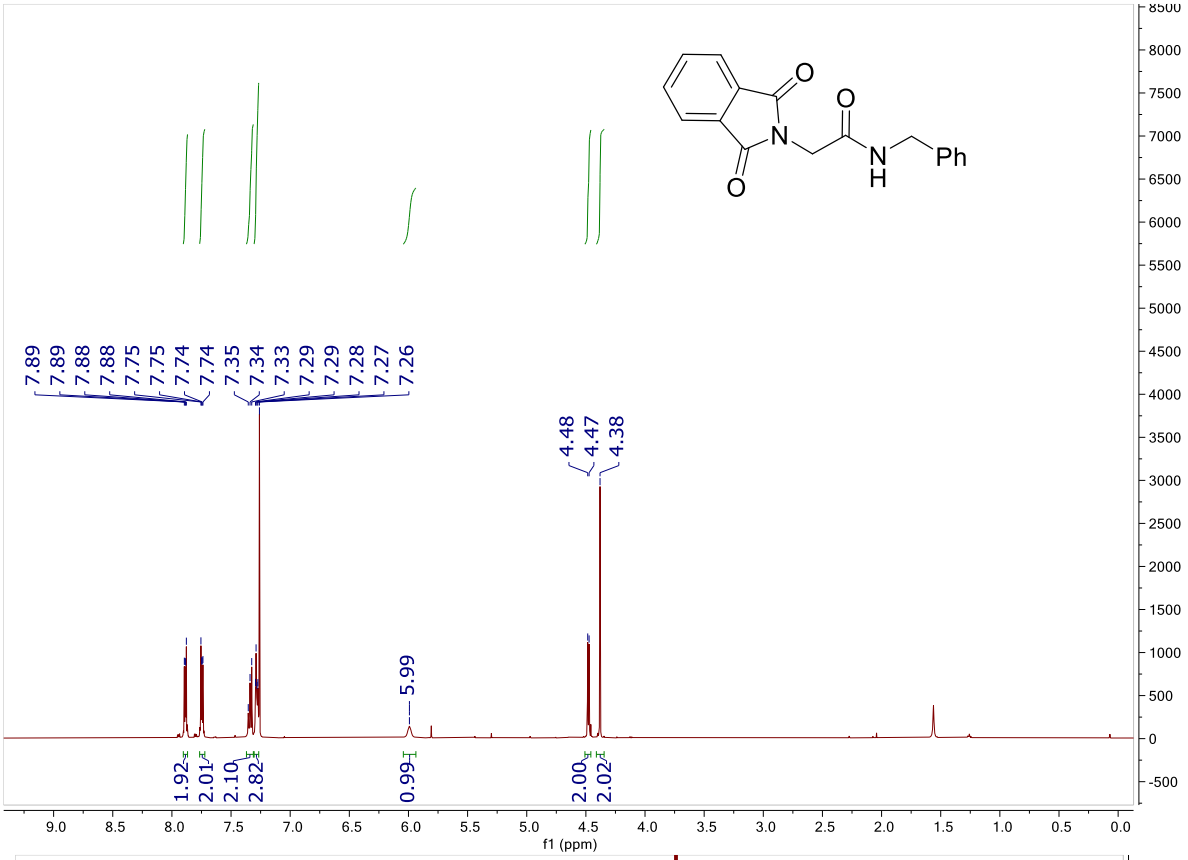
***In situ* ^{1}H, ^{13}C and ^{19}F NMR data for 4l.**

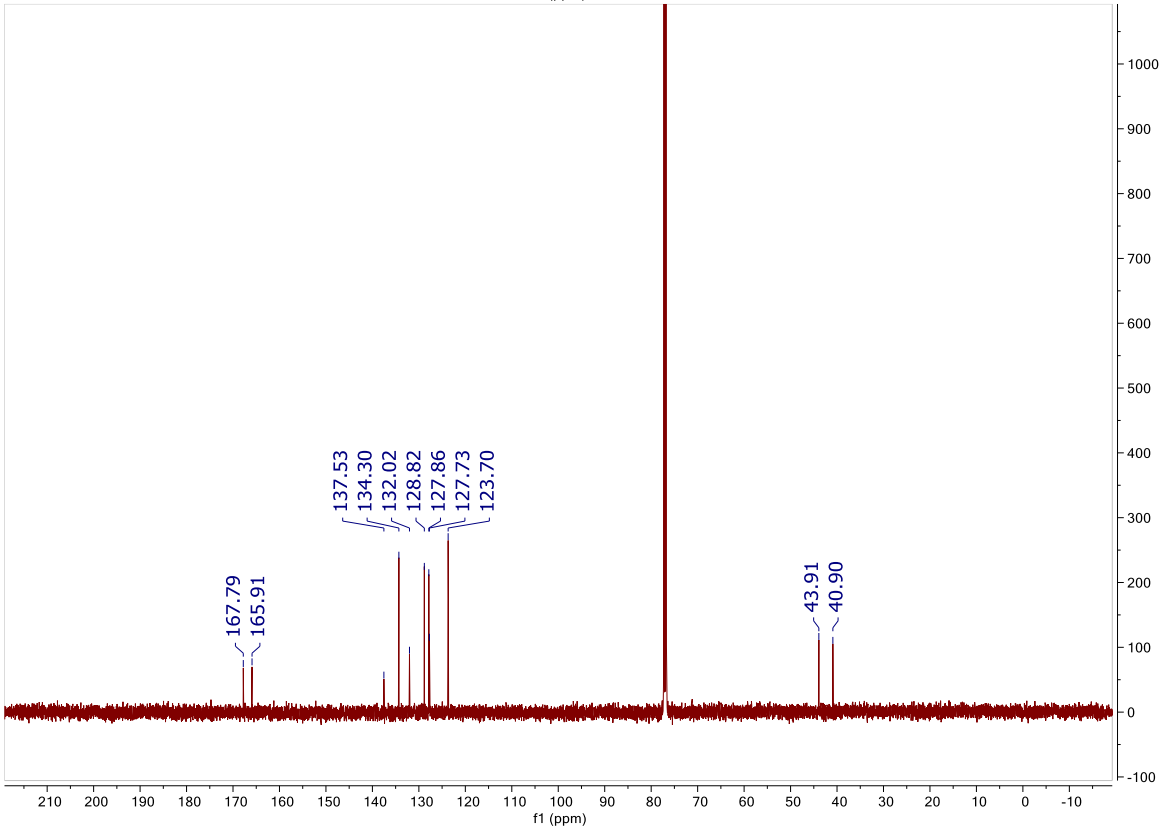




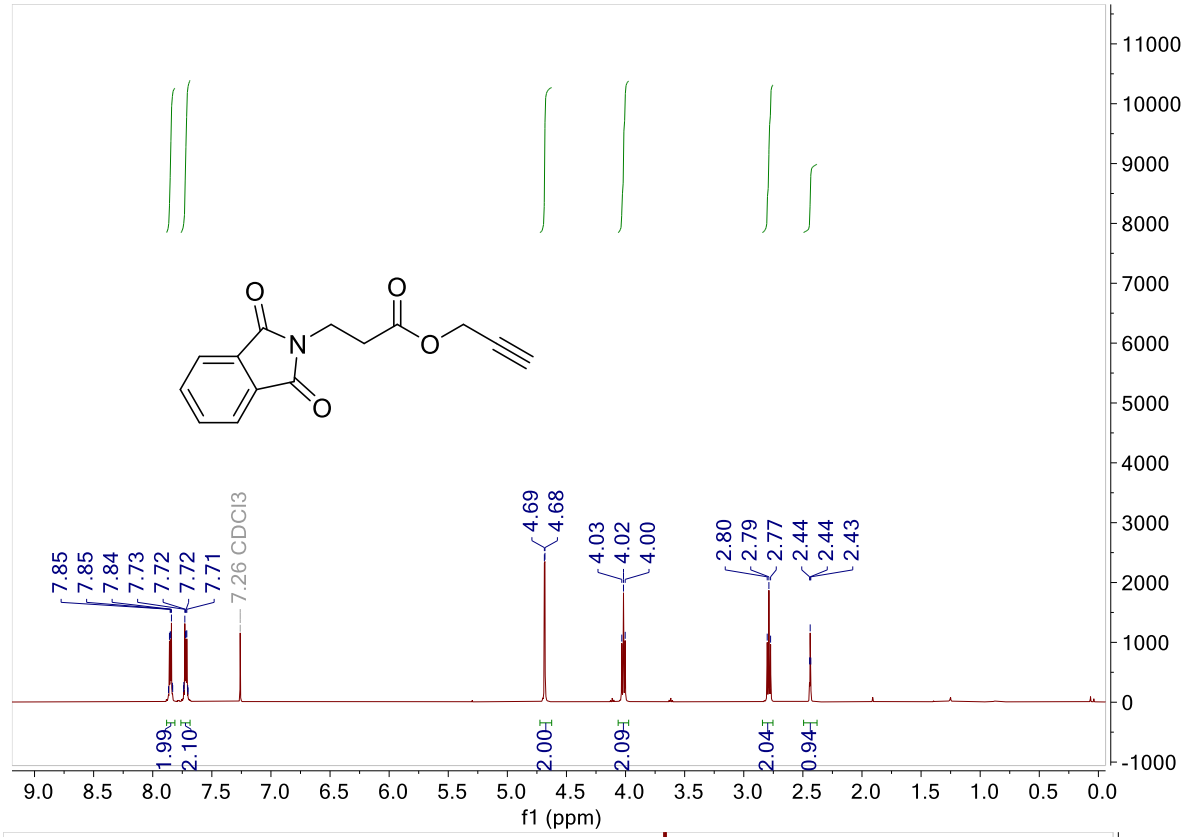

31.69
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
110
90
70
50
30
10
-10
-30
-50
-70
-90
-110
f1 (ppm)

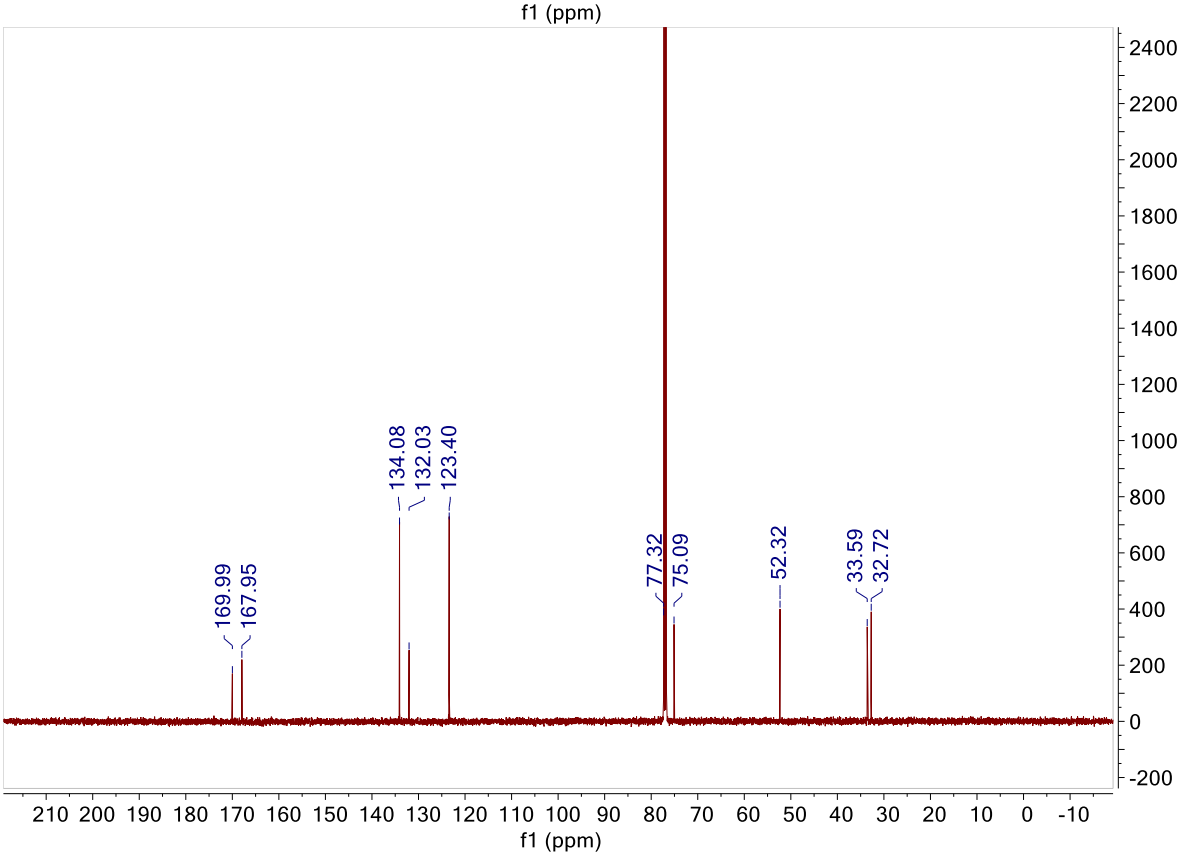
^{1}H and ^{13}C NMR data for 7l.



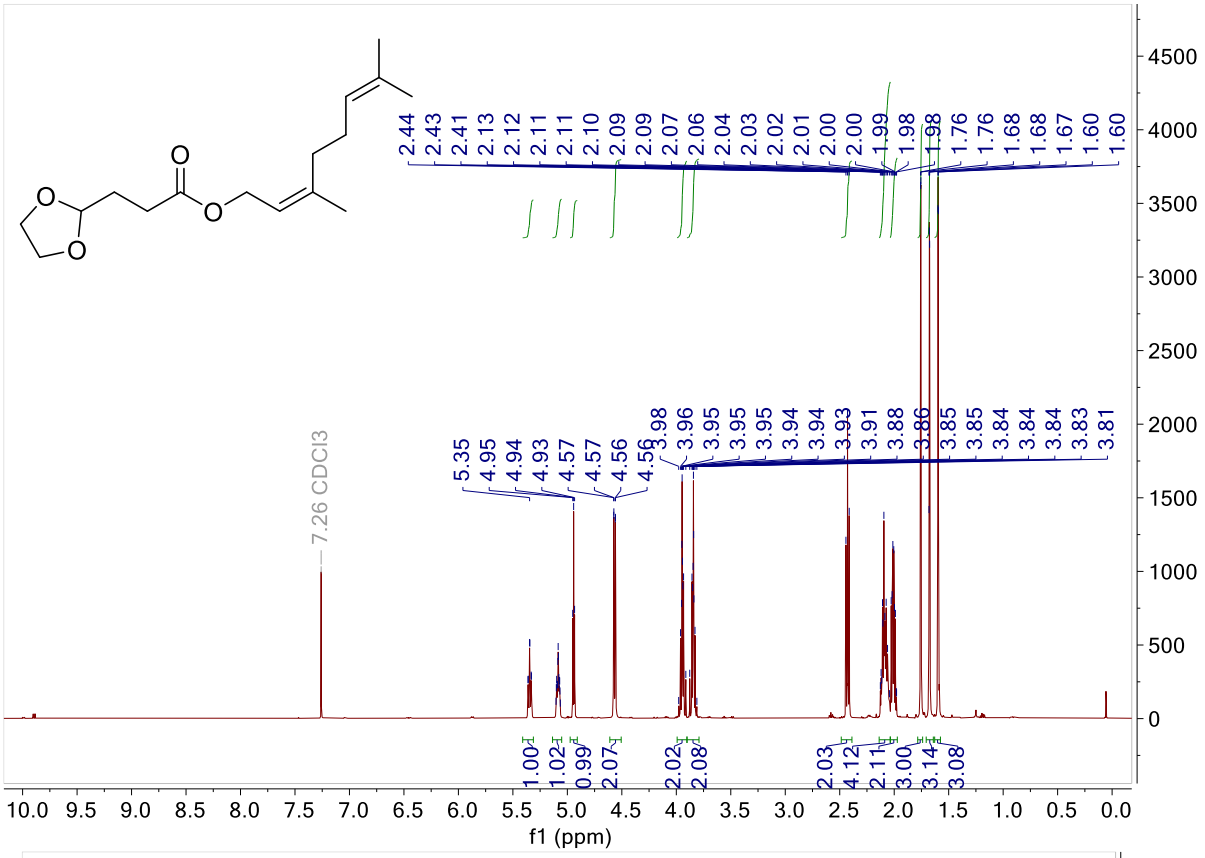


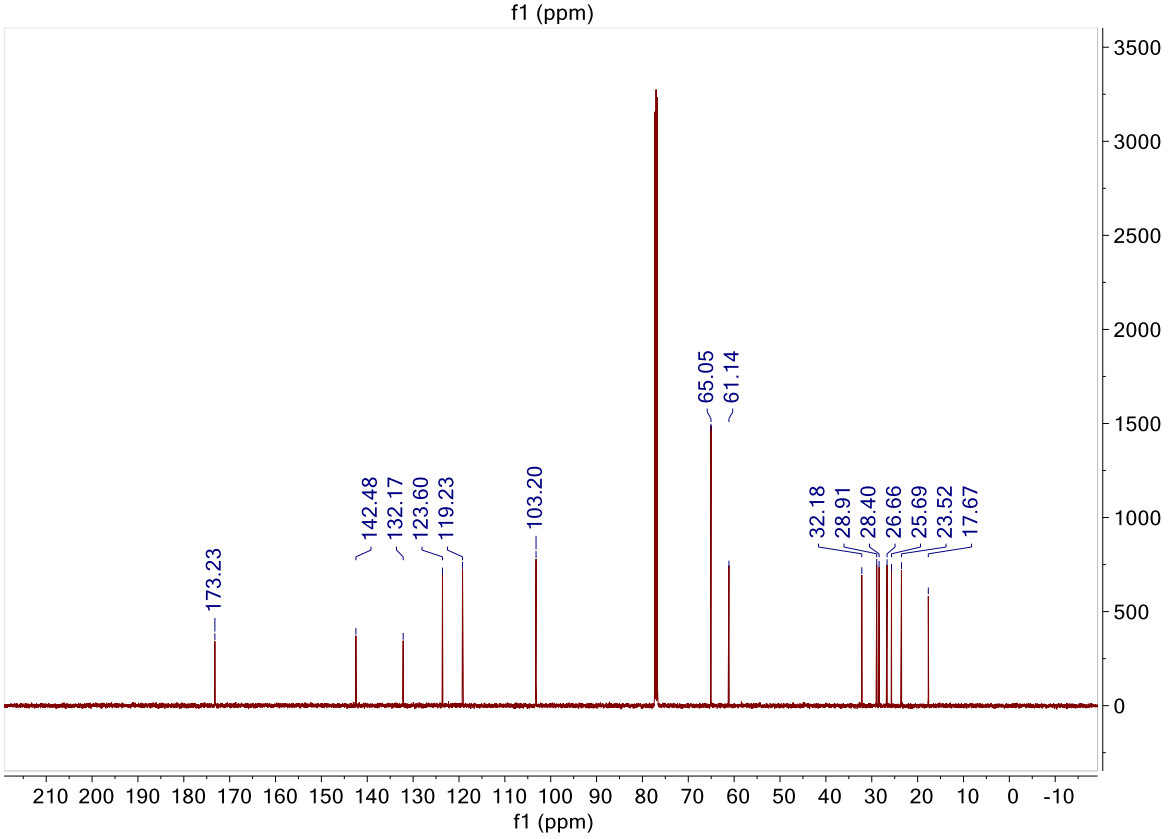
^{1}H and ^{13}C NMR data for 4m.



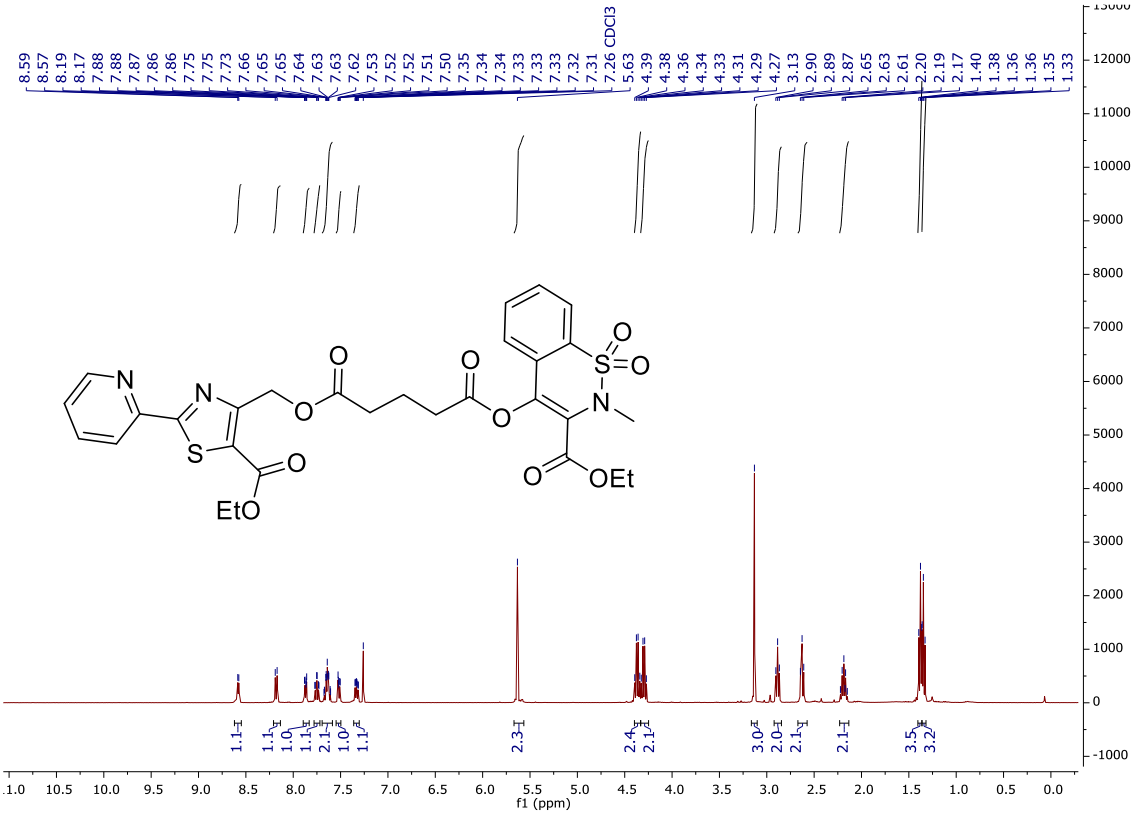


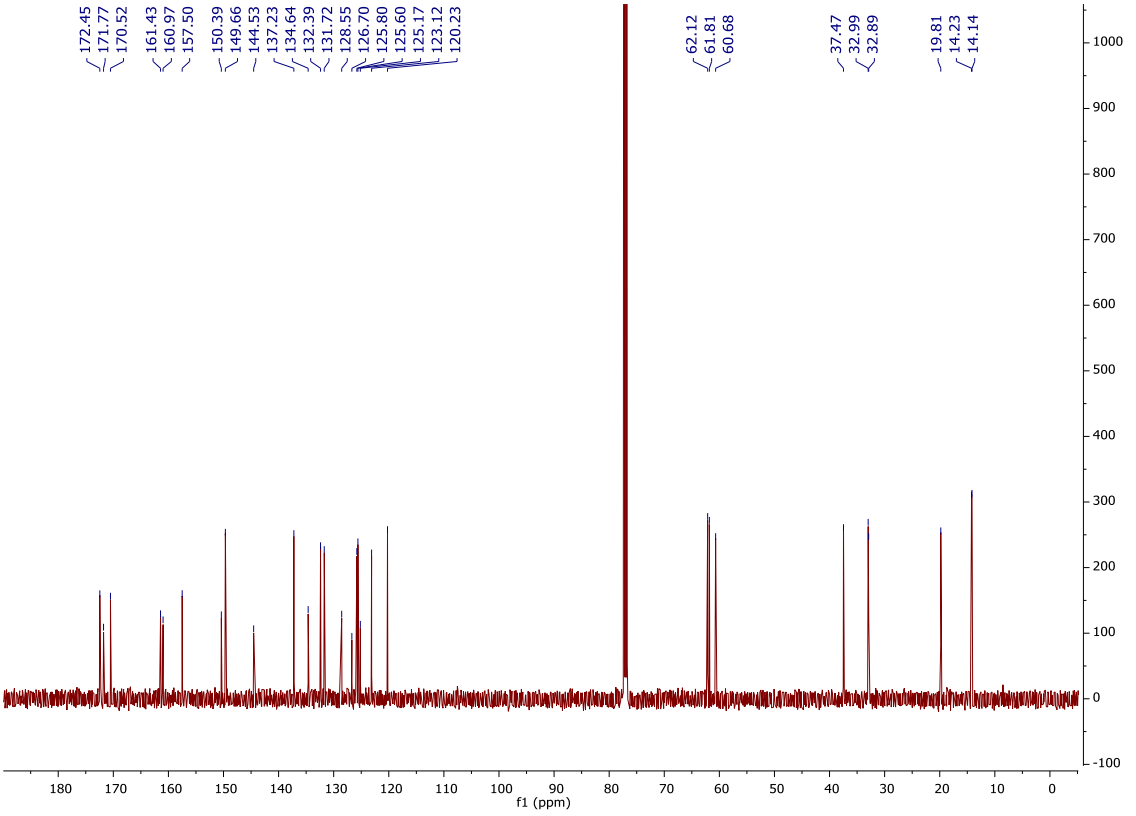
^{1}H and ^{13}C NMR data for 4n.



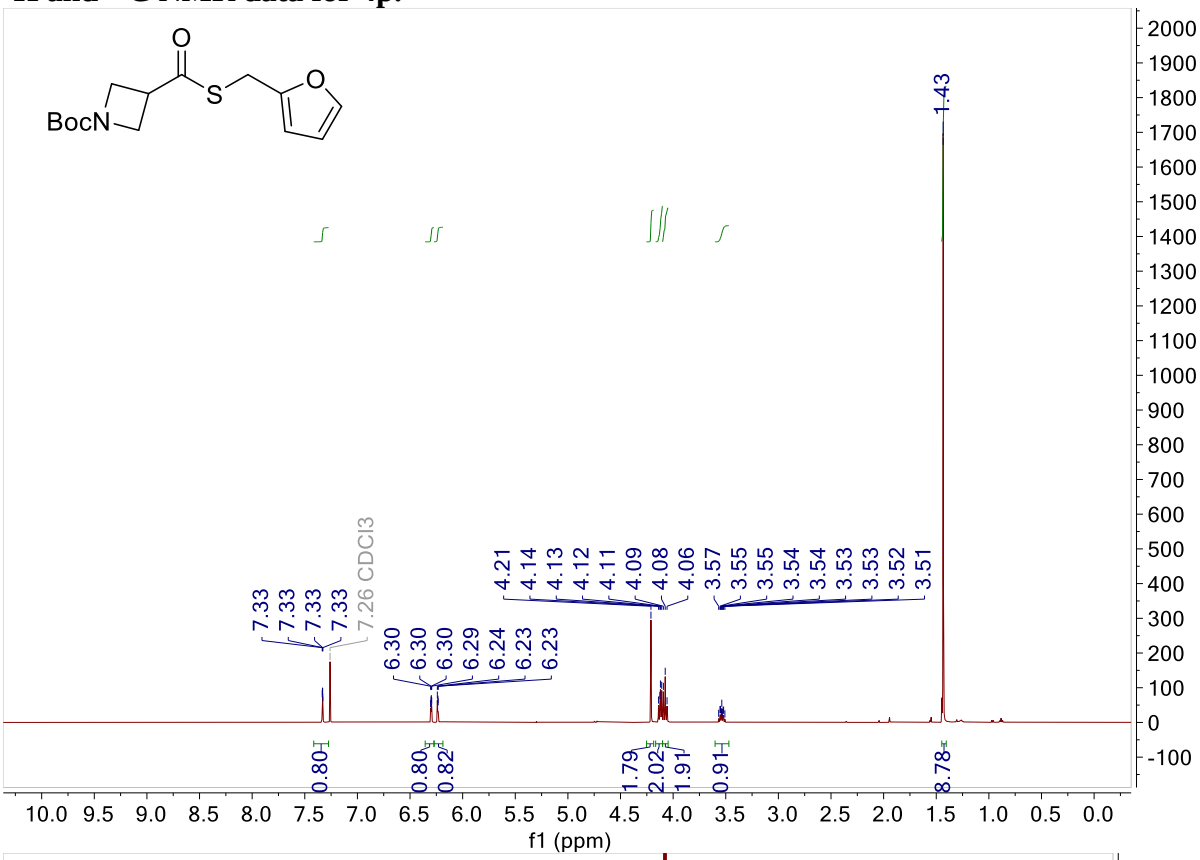


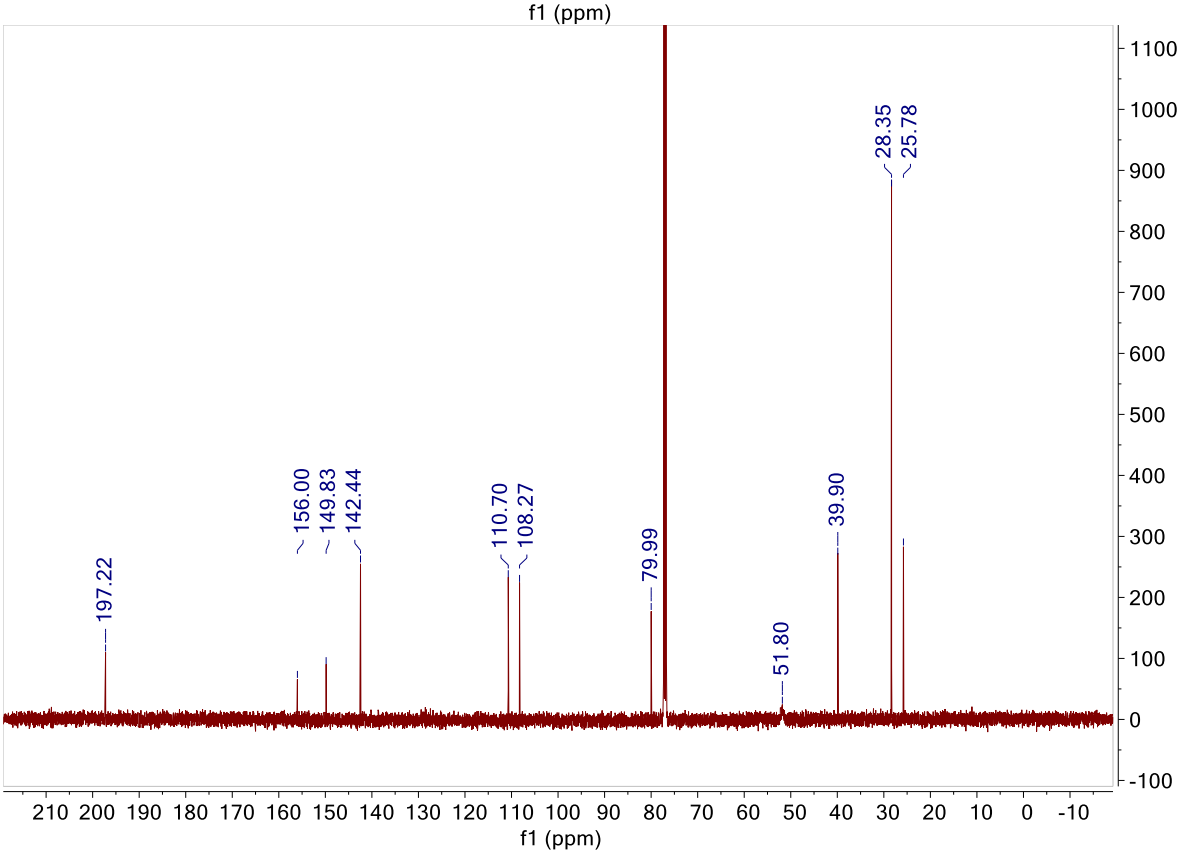
^{1}H and ^{13}C NMR data for 4o.



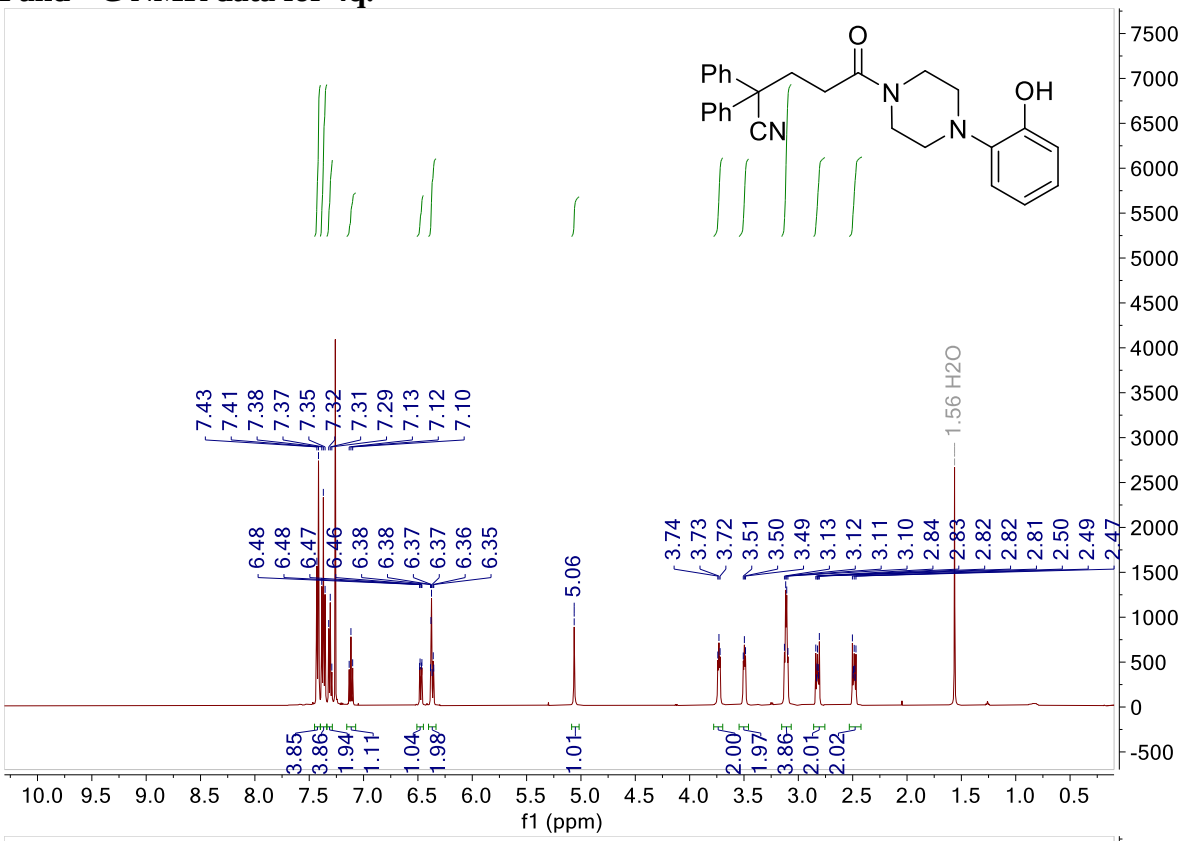


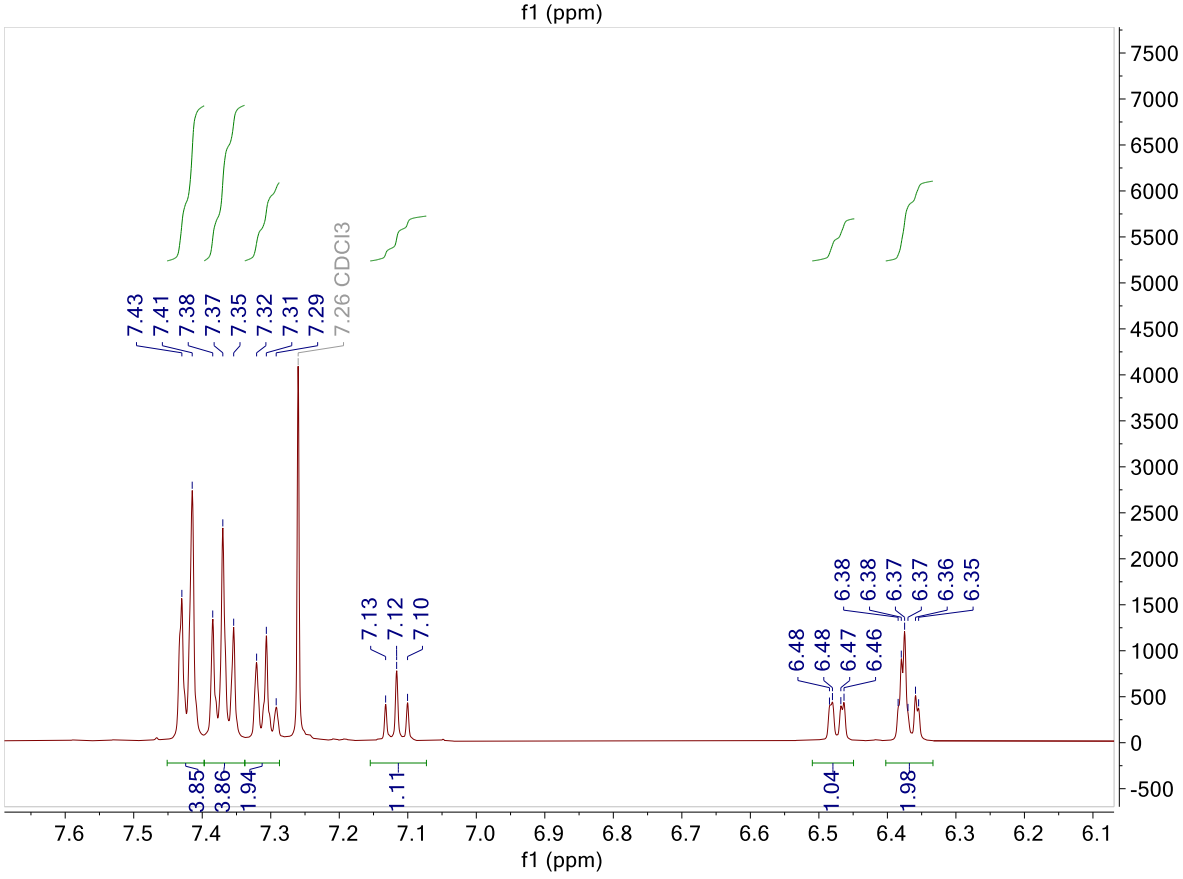
^{1}H and ^{13}C NMR data for 4p.

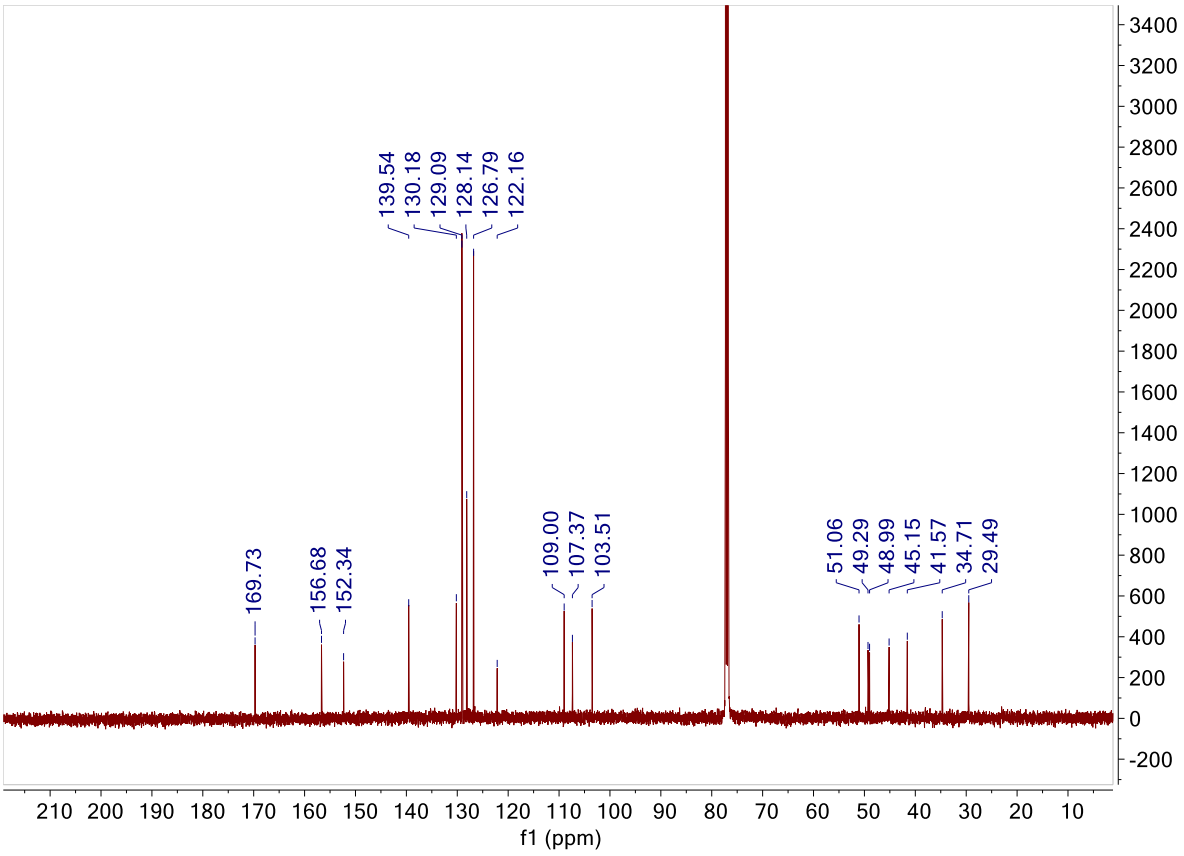




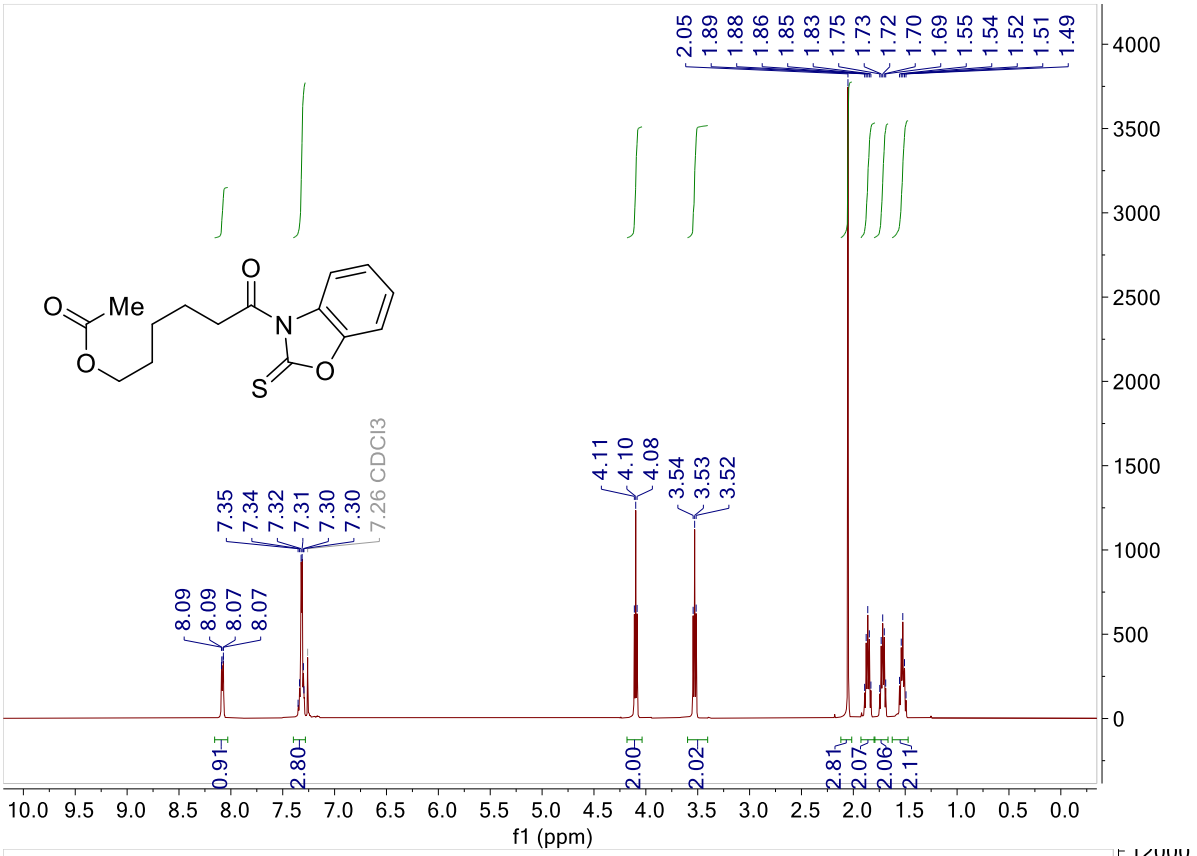
^{1}H and ^{13}C NMR data for 4q.

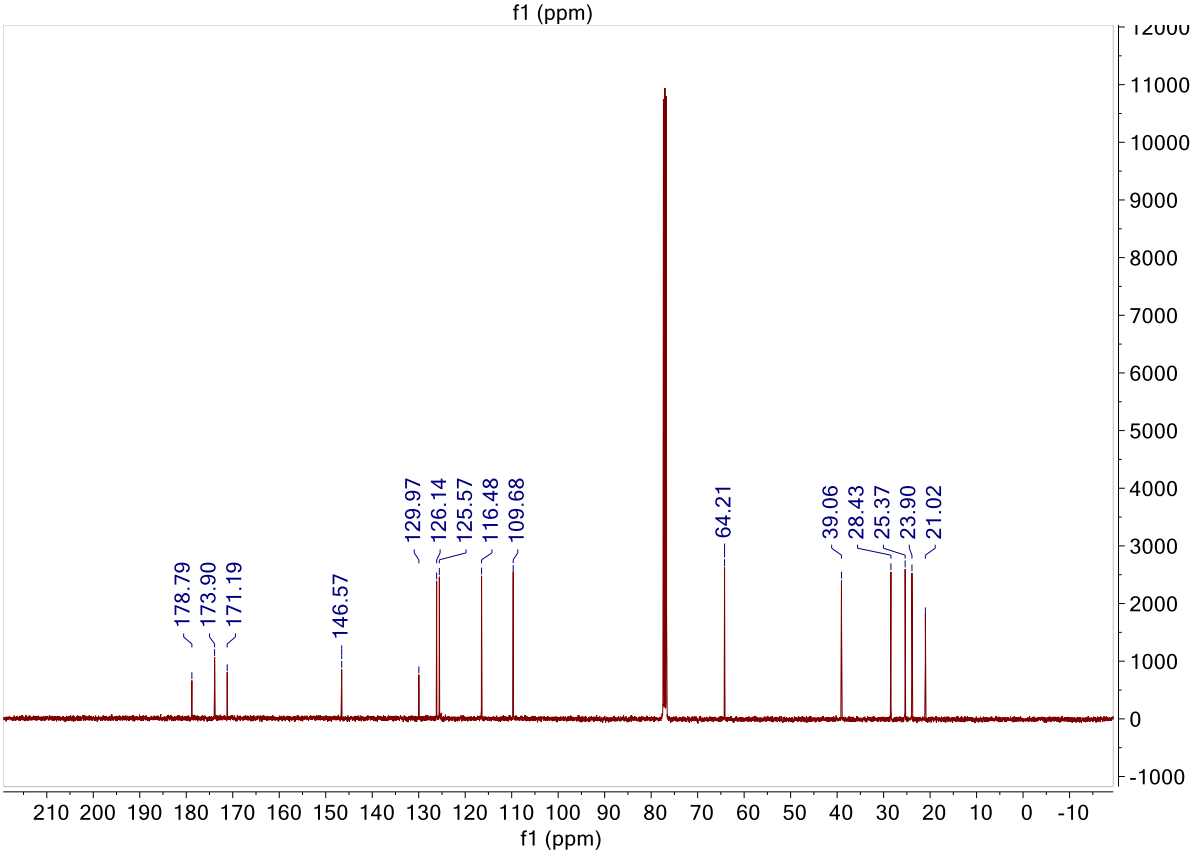




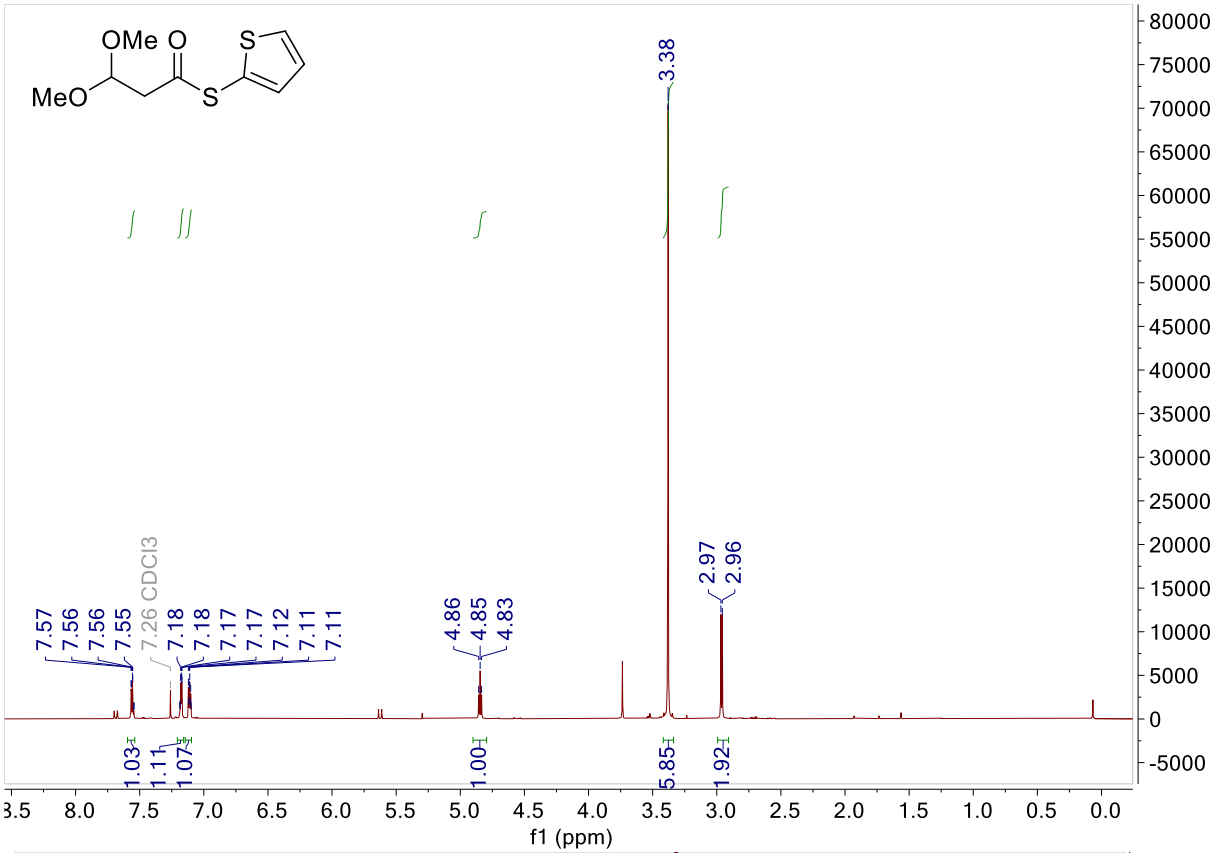

139.54
130.18
129.09
128.14
126.79
122.16
169.73
156.68
152.34
109.00
107.37
103.51
51.06
49.29
48.99
45.15
41.57
34.71
29.49
f1 (ppm)

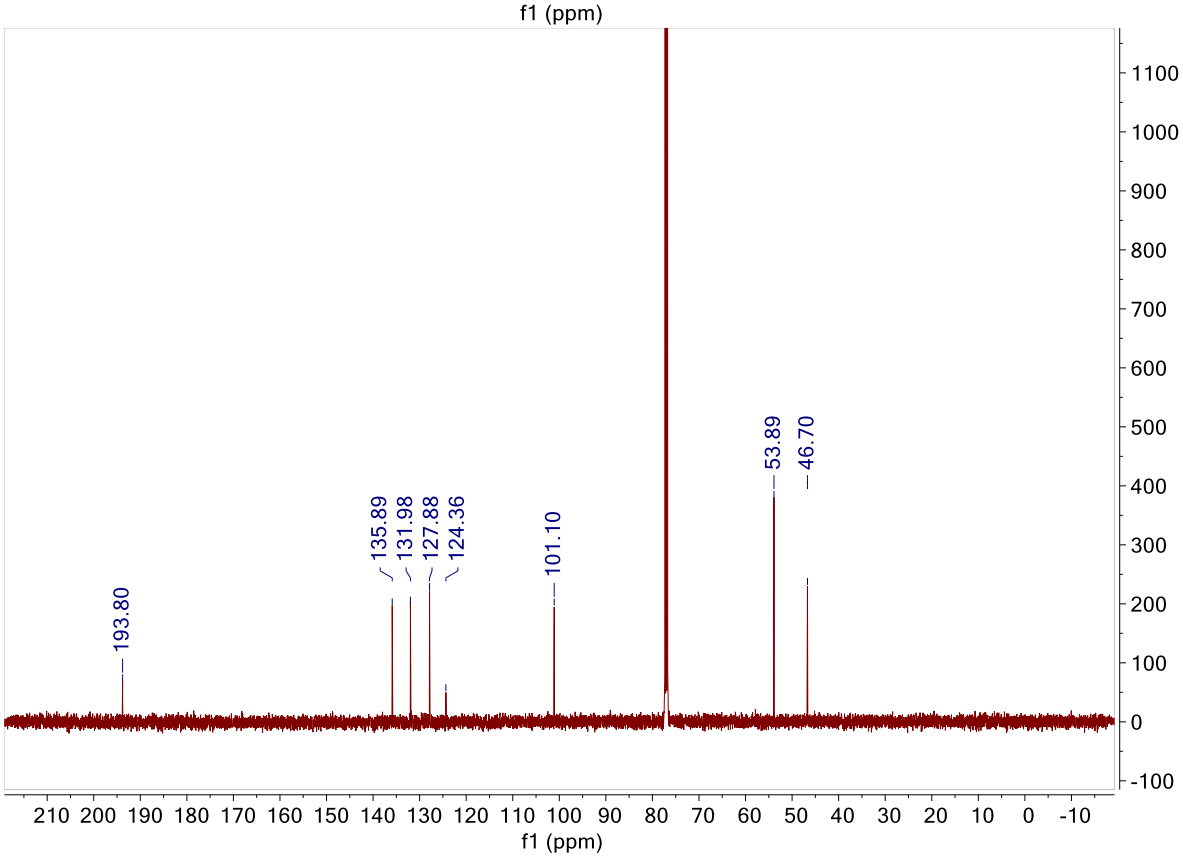
^{1}H and ^{13}C NMR data for 4r.



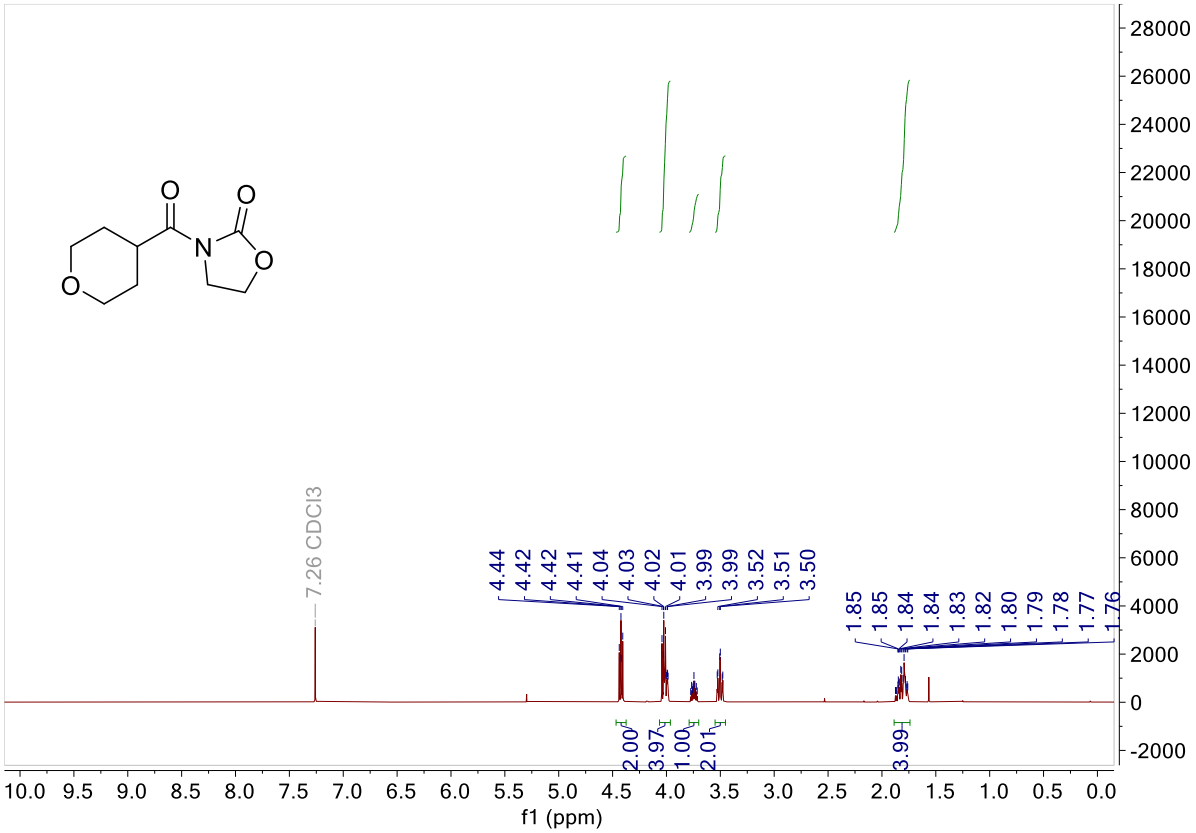


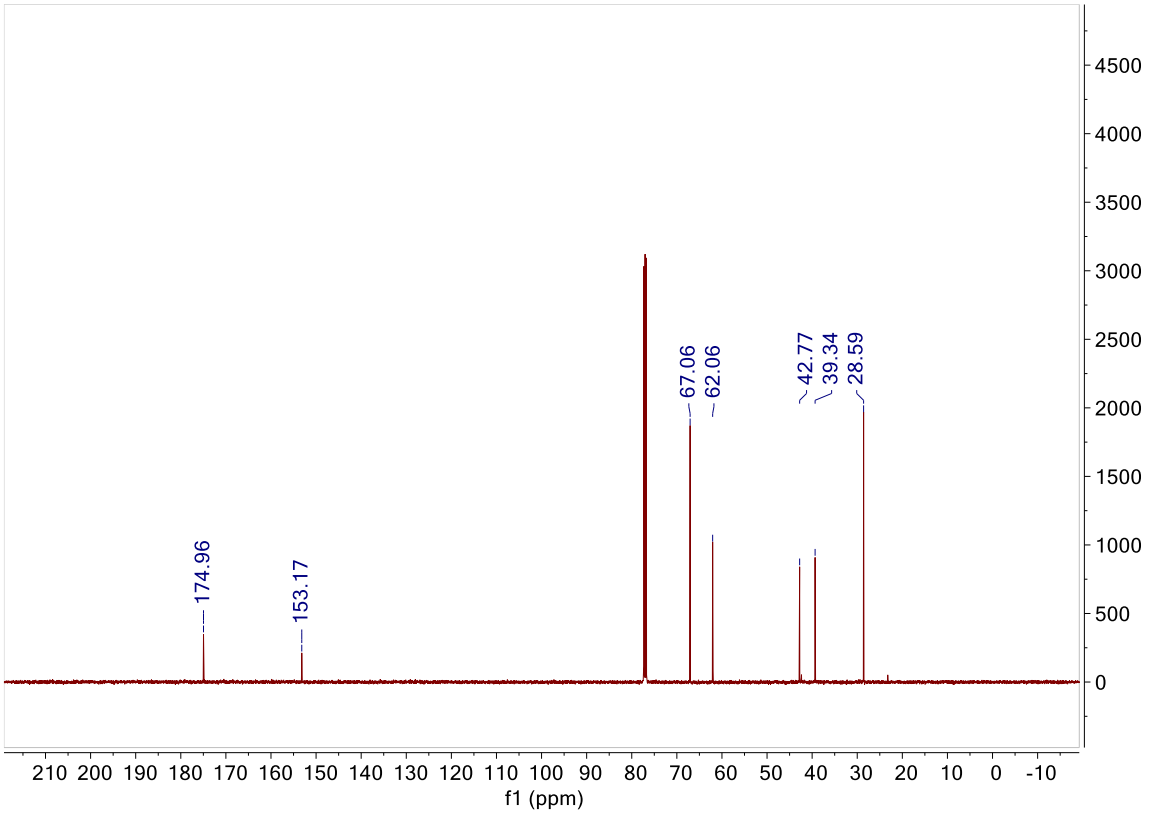
^{1}H and ^{13}C NMR data for 4s.



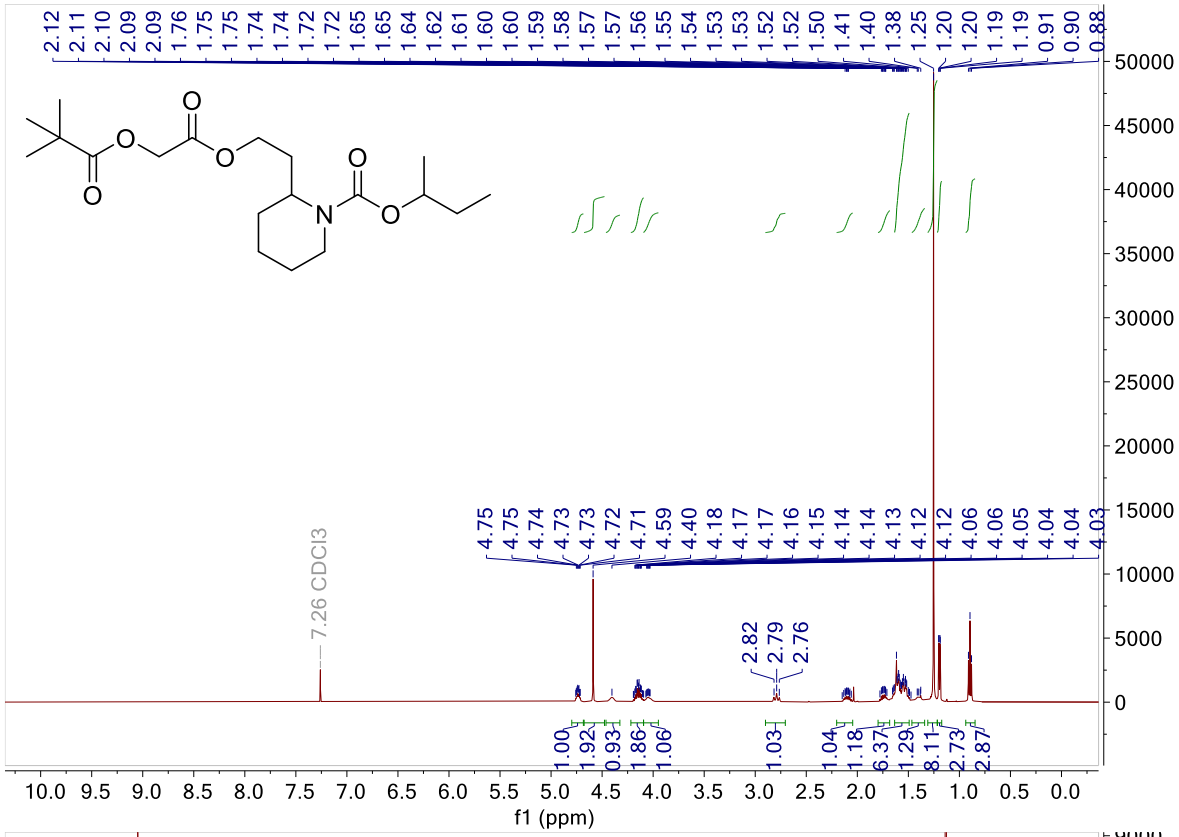


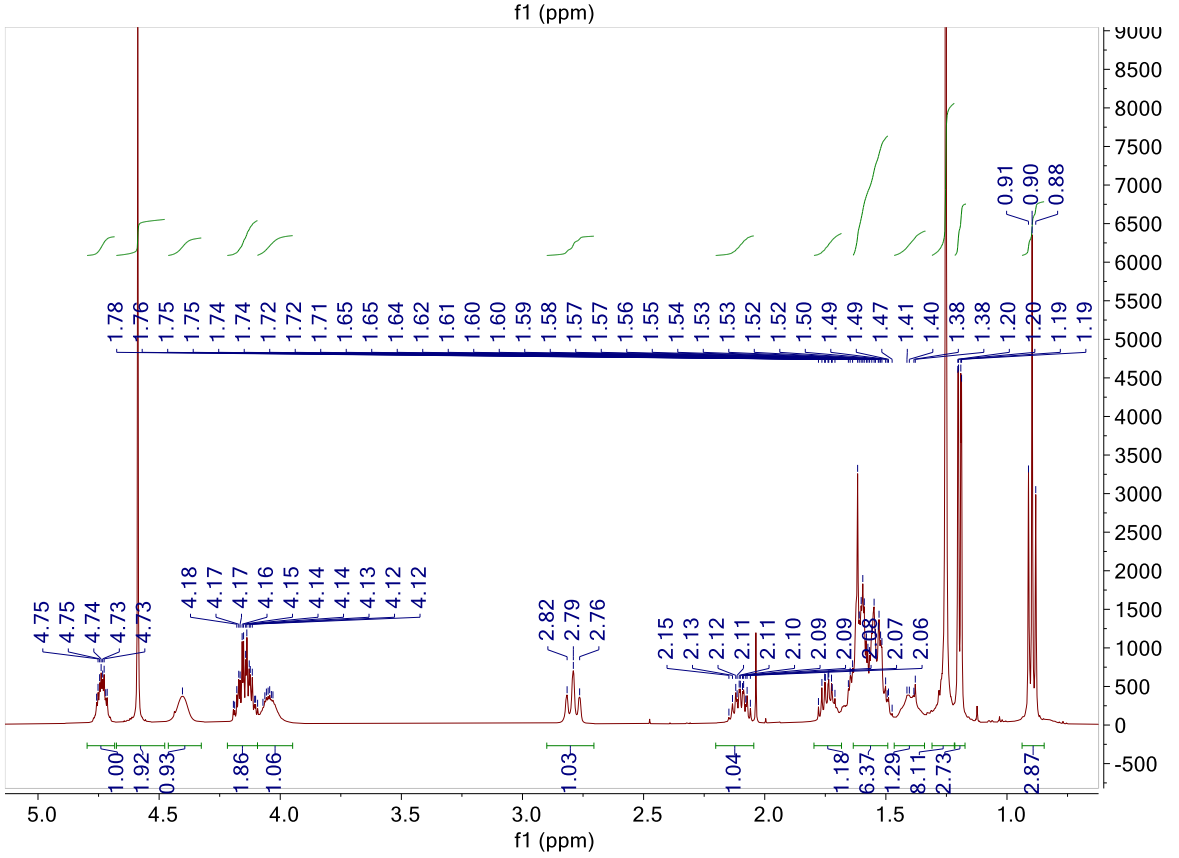
^{1}H and ^{13}C NMR data for 4t.

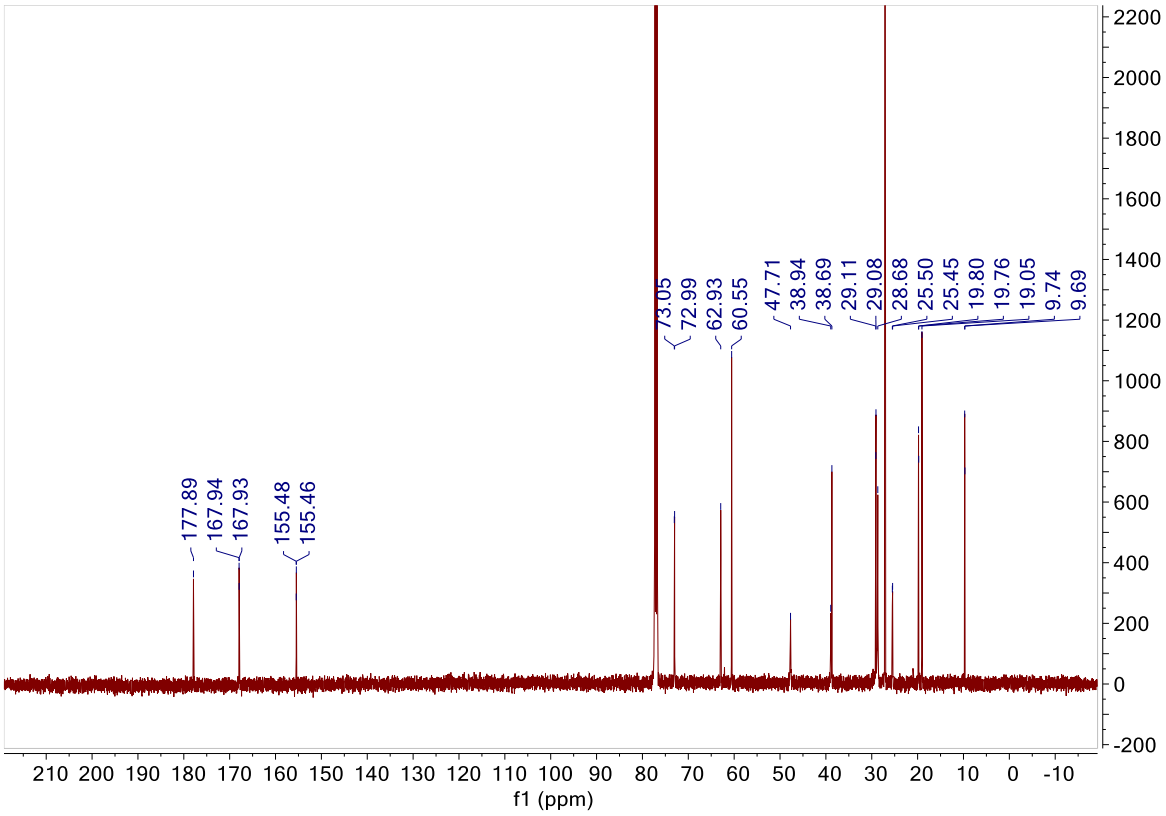




^{1}H and ^{13}C NMR data for 4u.



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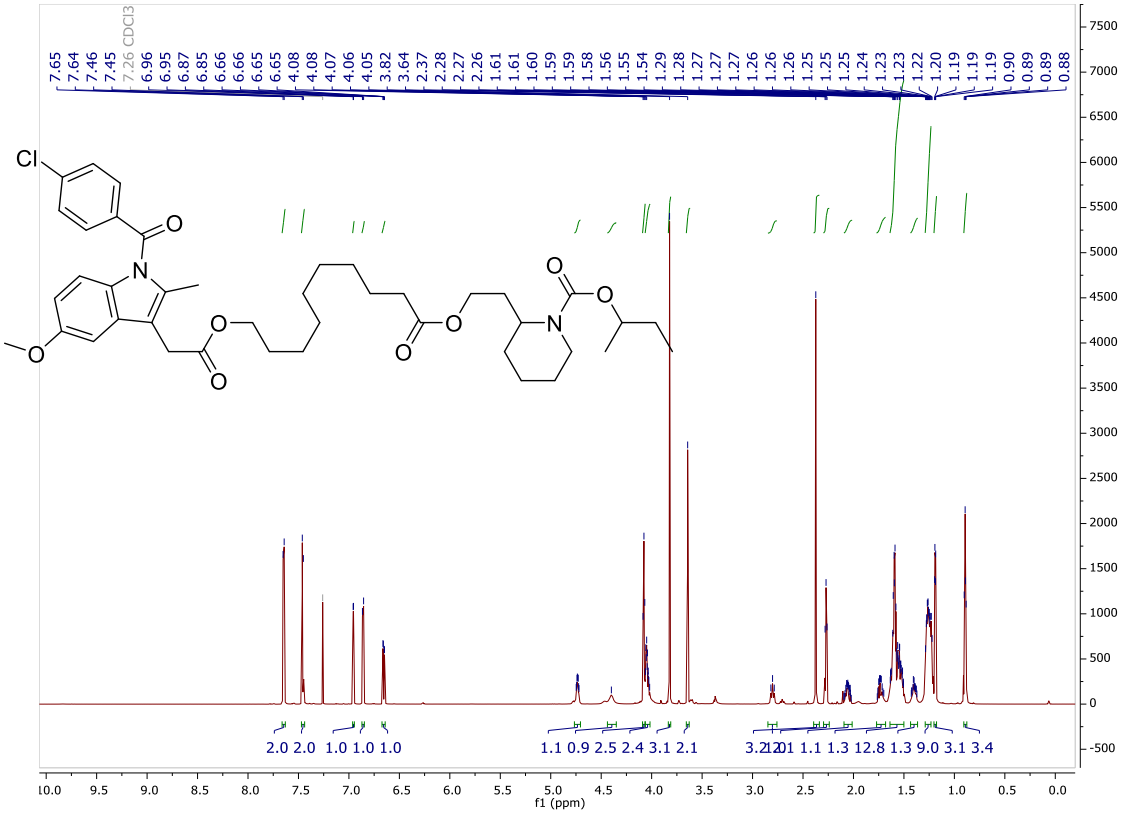
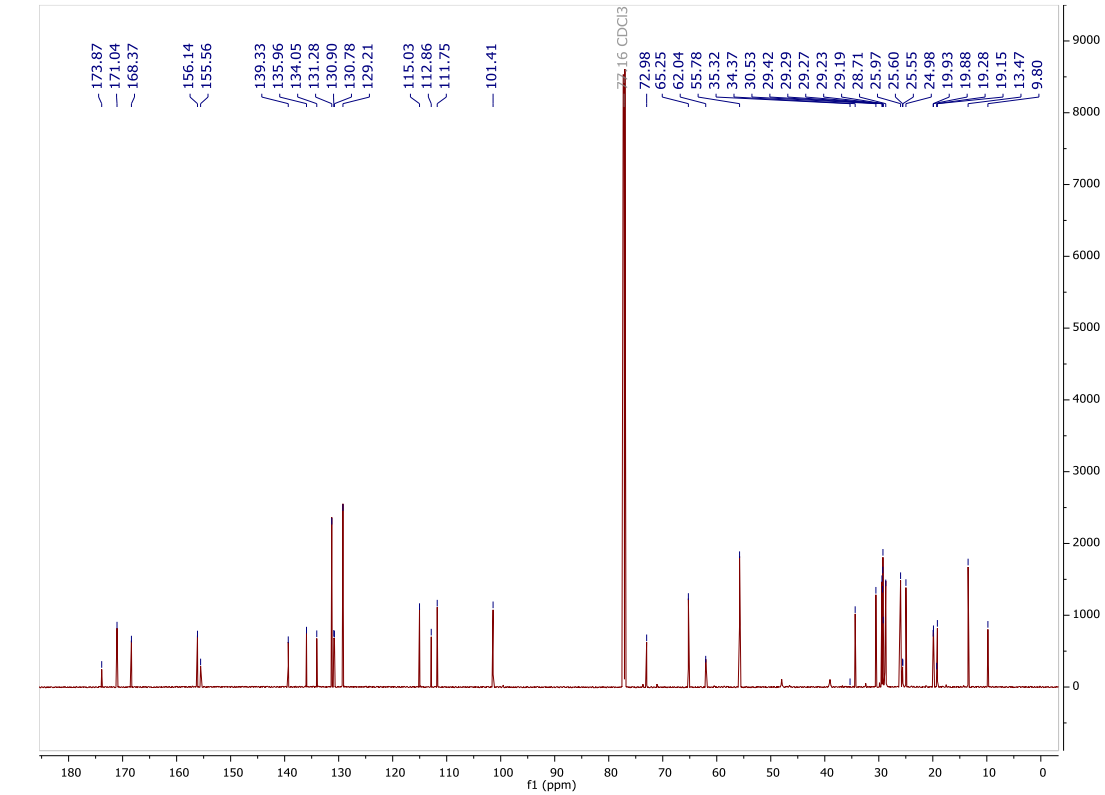
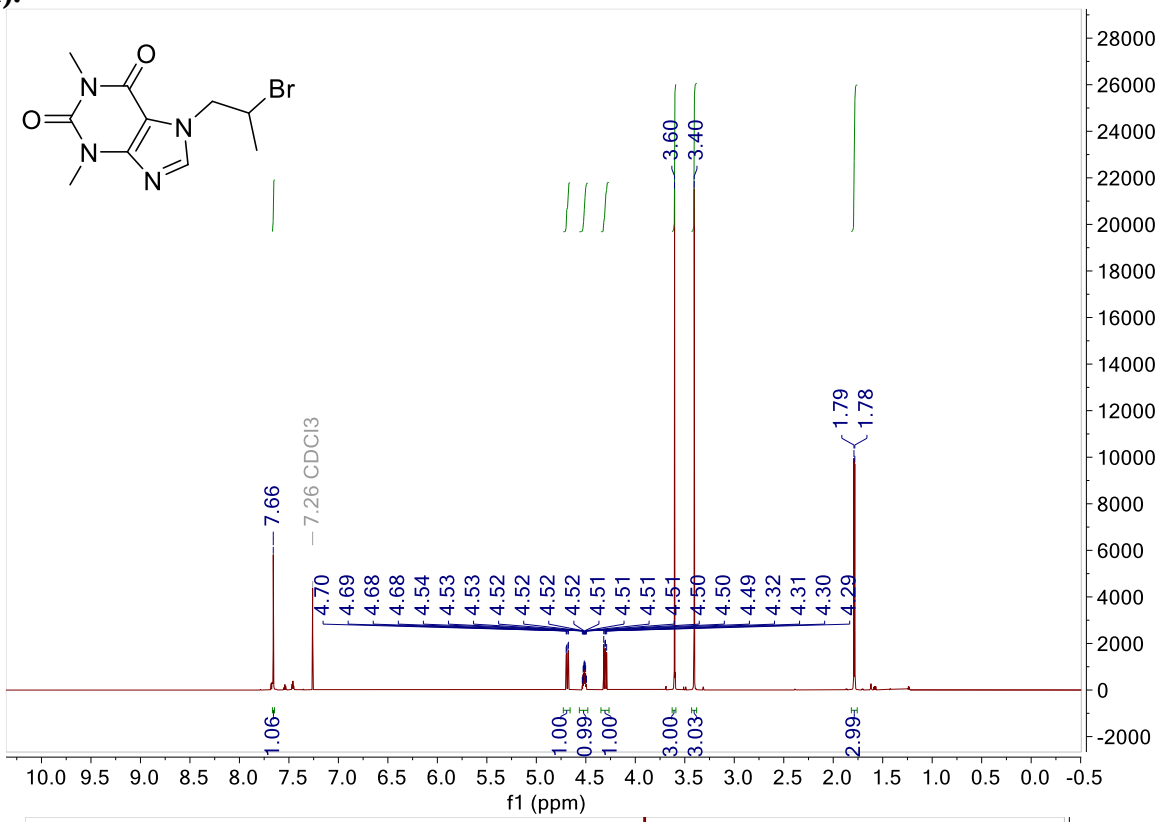
167.93
155.48
155.46
73.05
72.99
62.93
60.55
47.71
38.94
38.69
29.11
29.08
28.68
25.50
25.45
19.80
19.76
19.05
9.74
9.69
f1 (ppm)

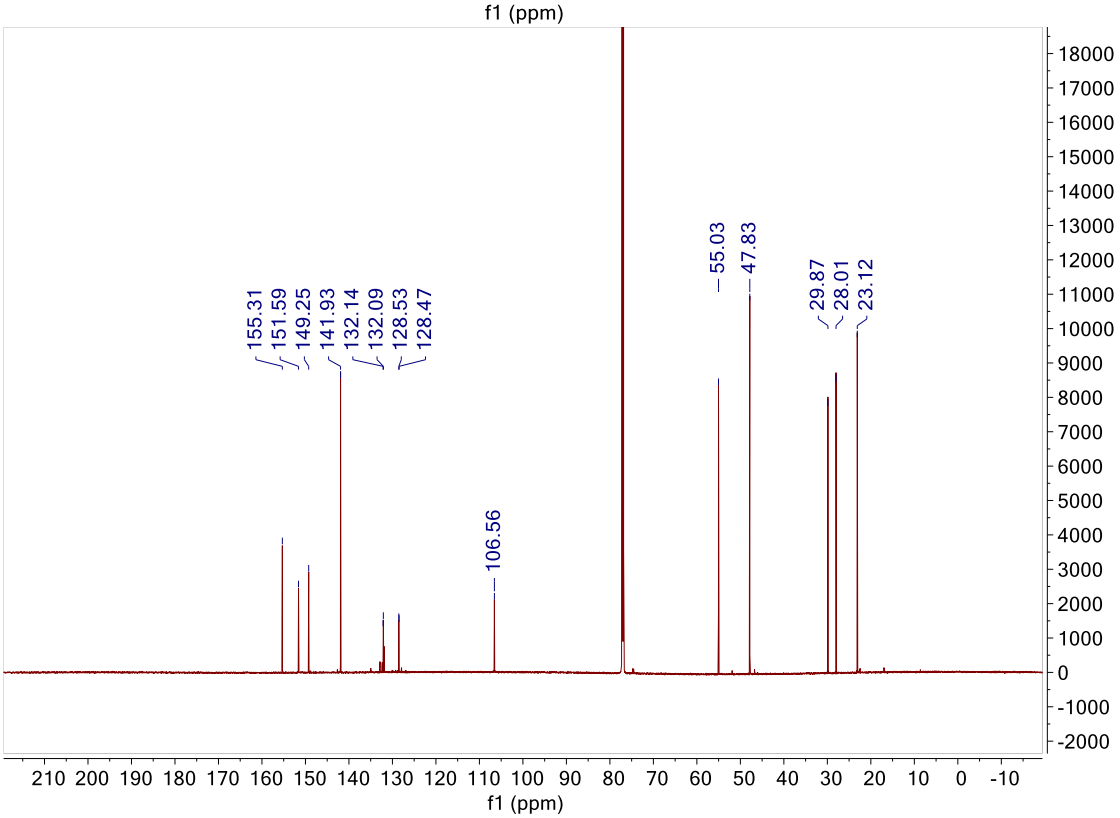
^{1}H and ^{13}C NMR data for 4v.



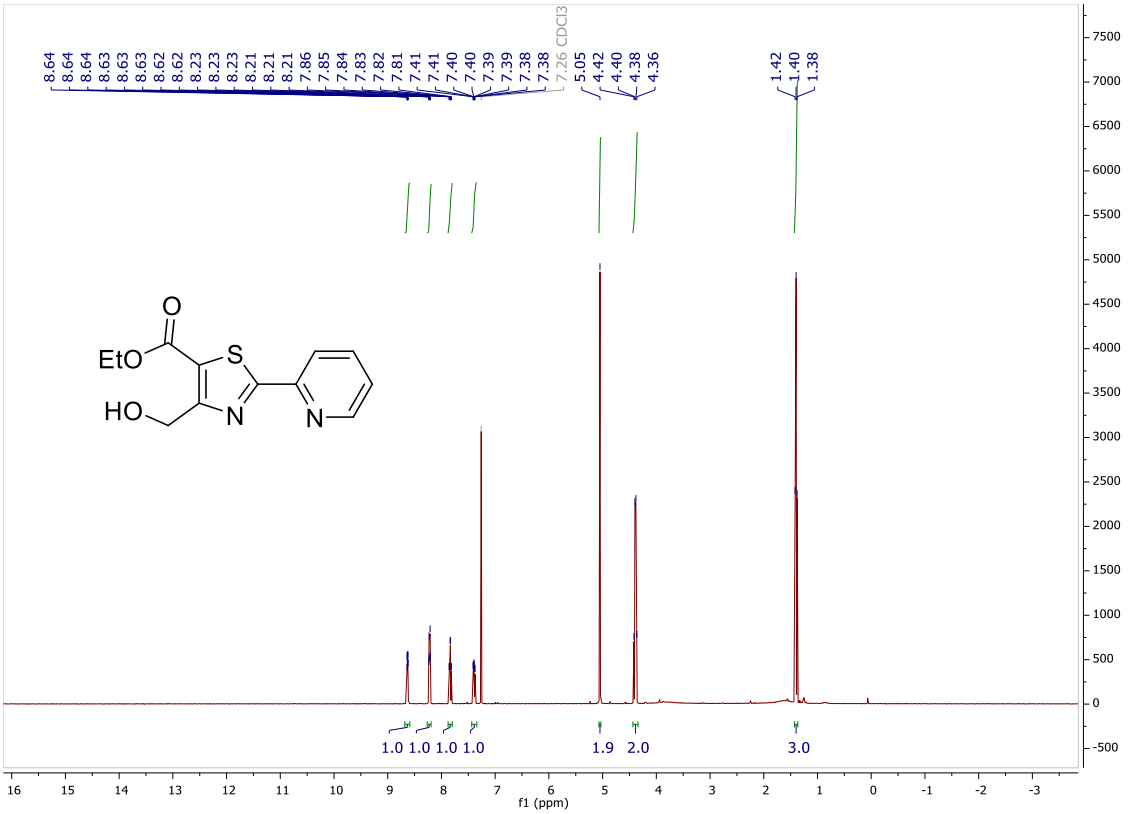


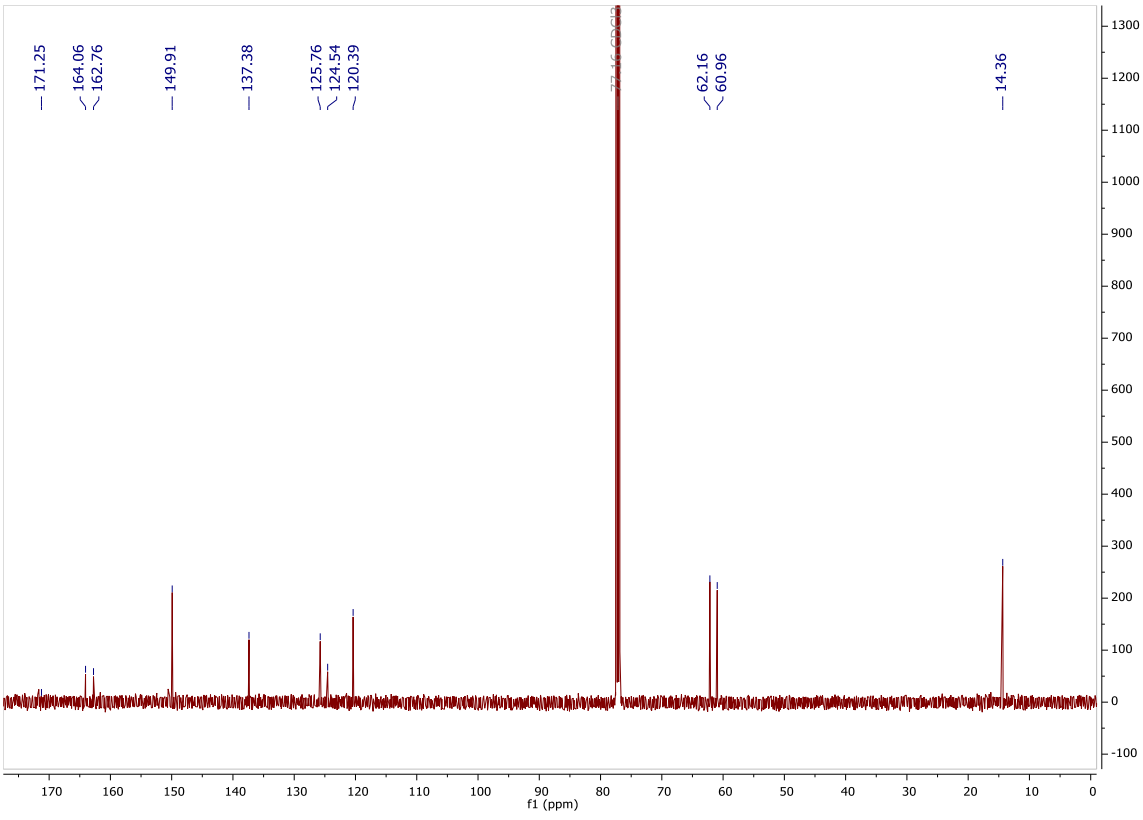
^{1}H and ^{13}C NMR data for 7-(2-bromopropyl)-1,3-dimethyl-3,7-dihydro-1H-purine-2,6-dione (S1).



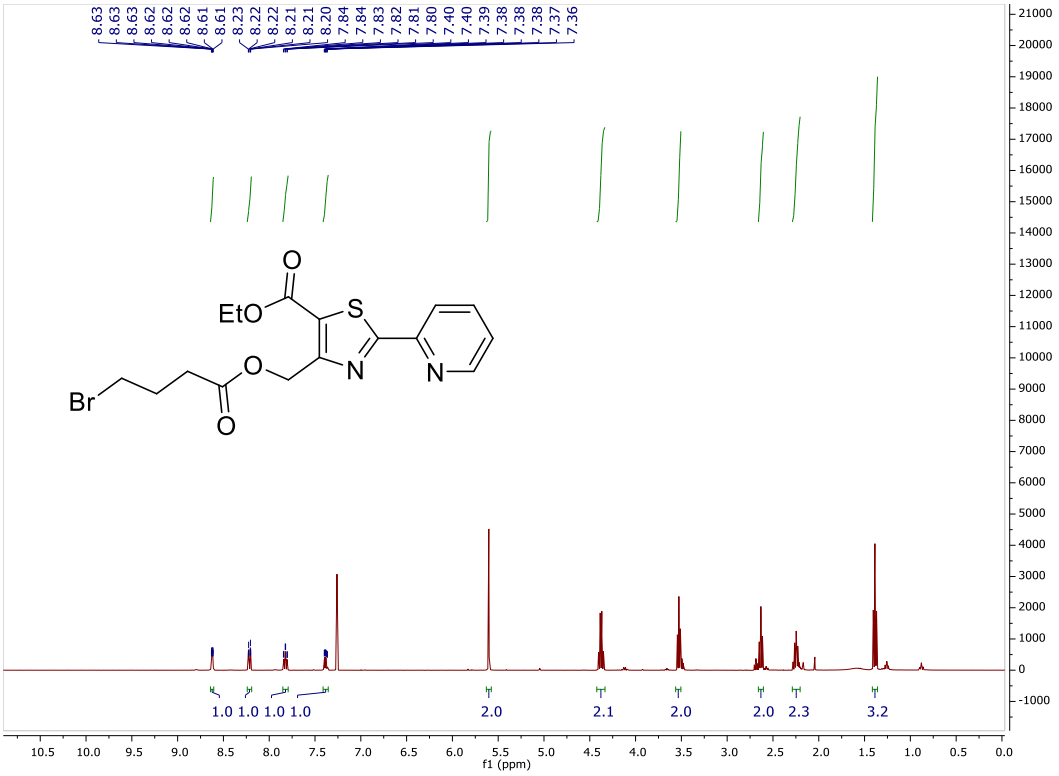


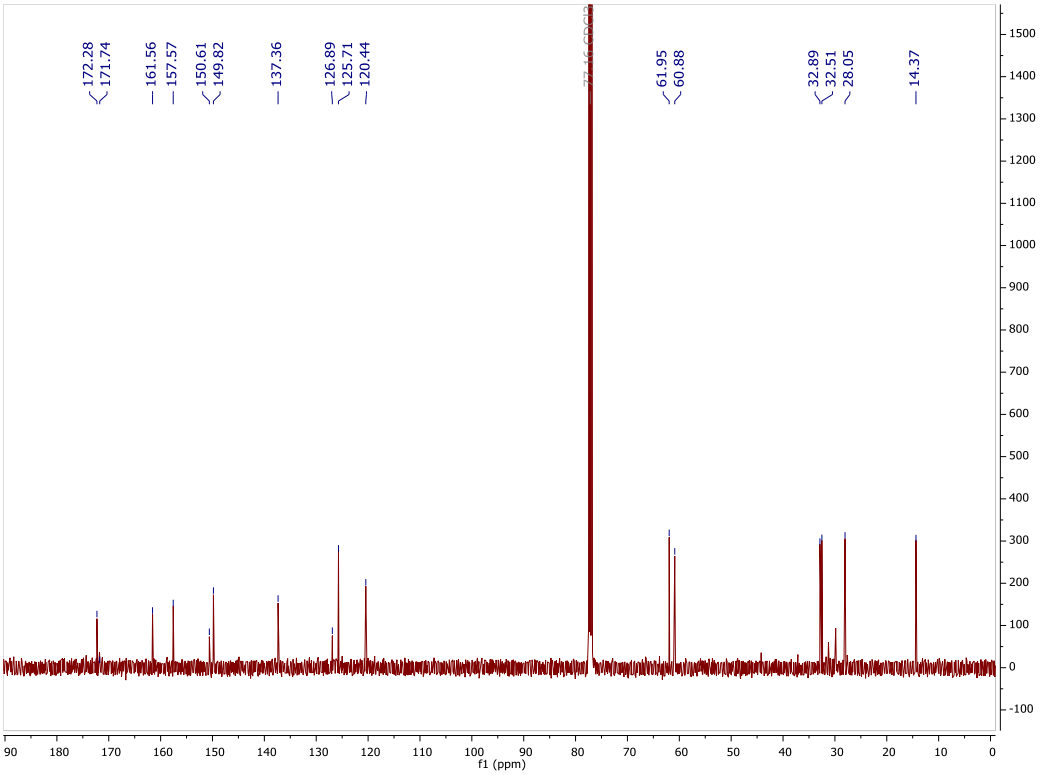
^{1}H and ^{13}C NMR data for S2.



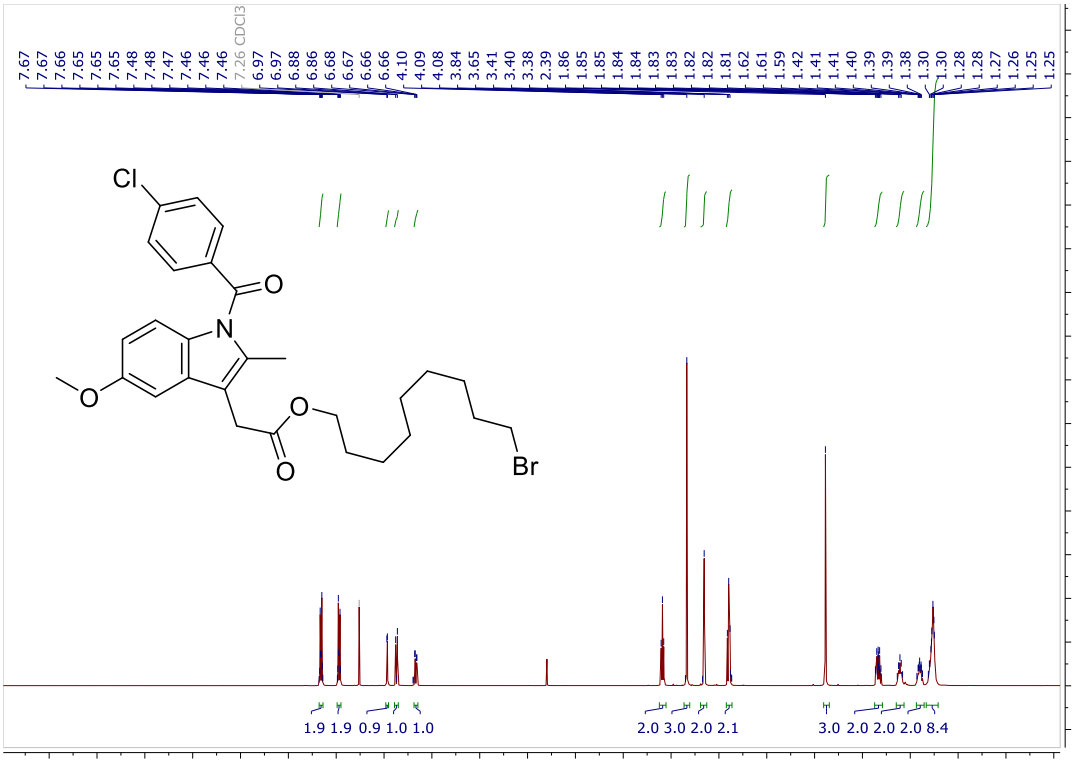


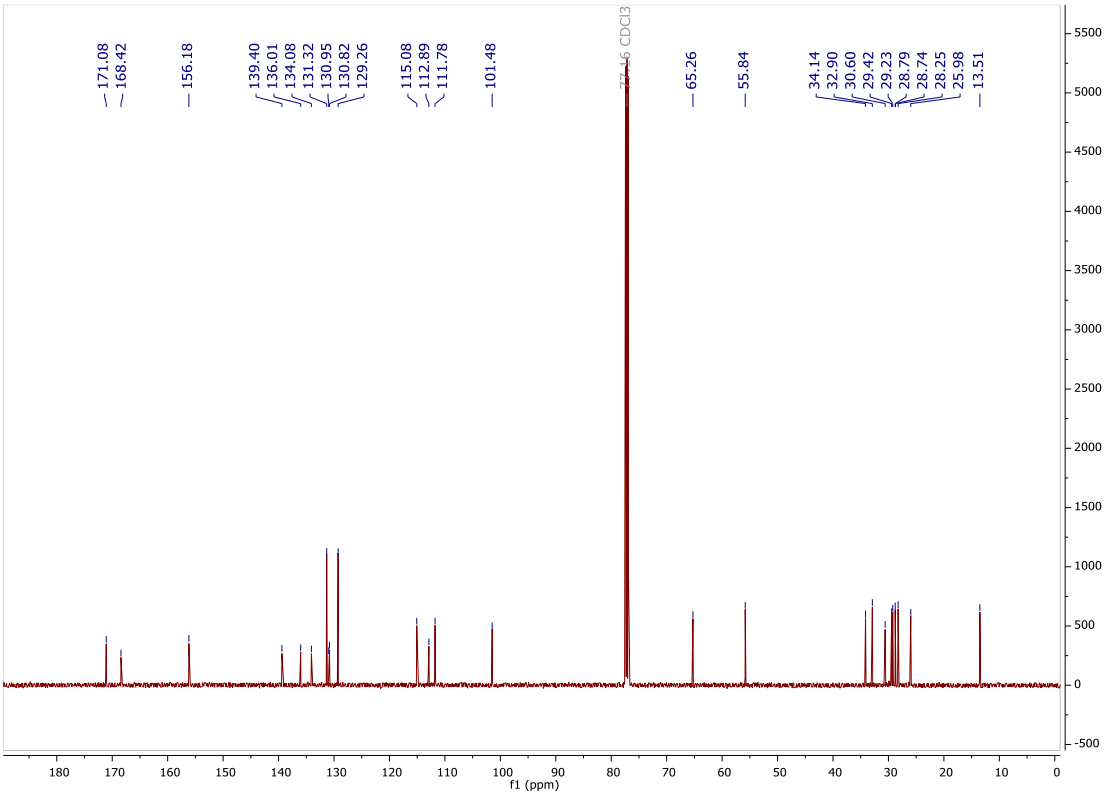
^{1}H and ^{13}C NMR data for S3.



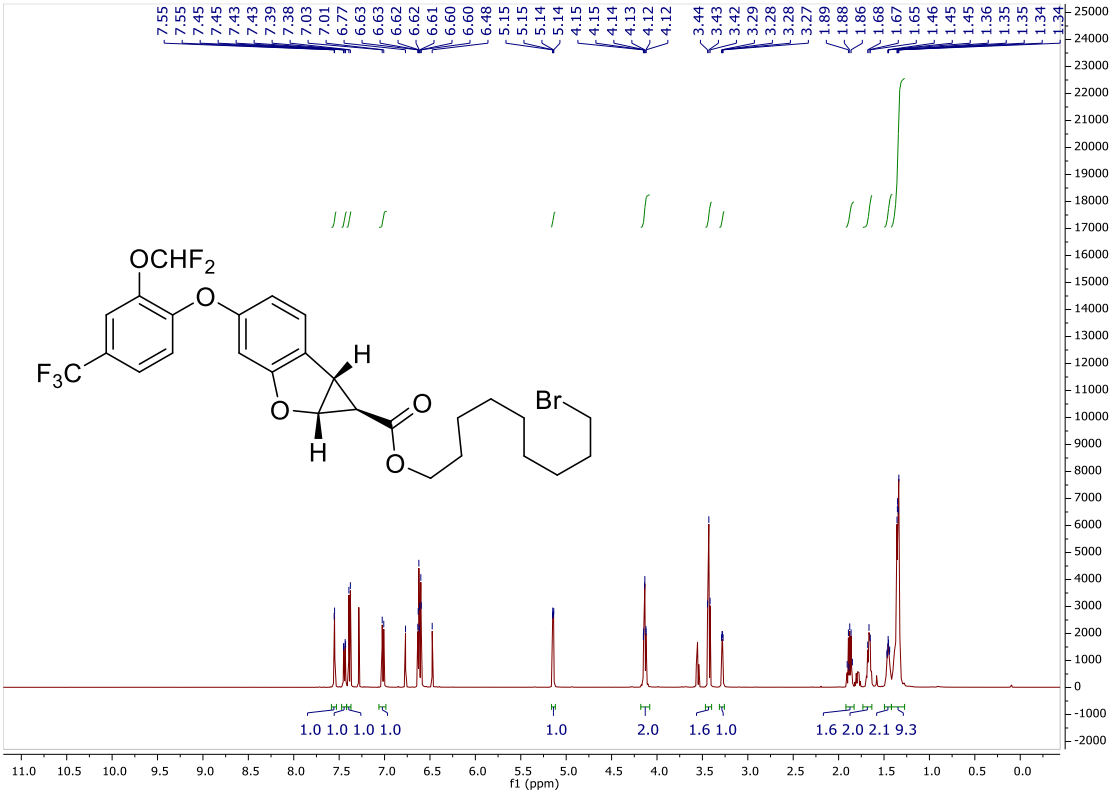


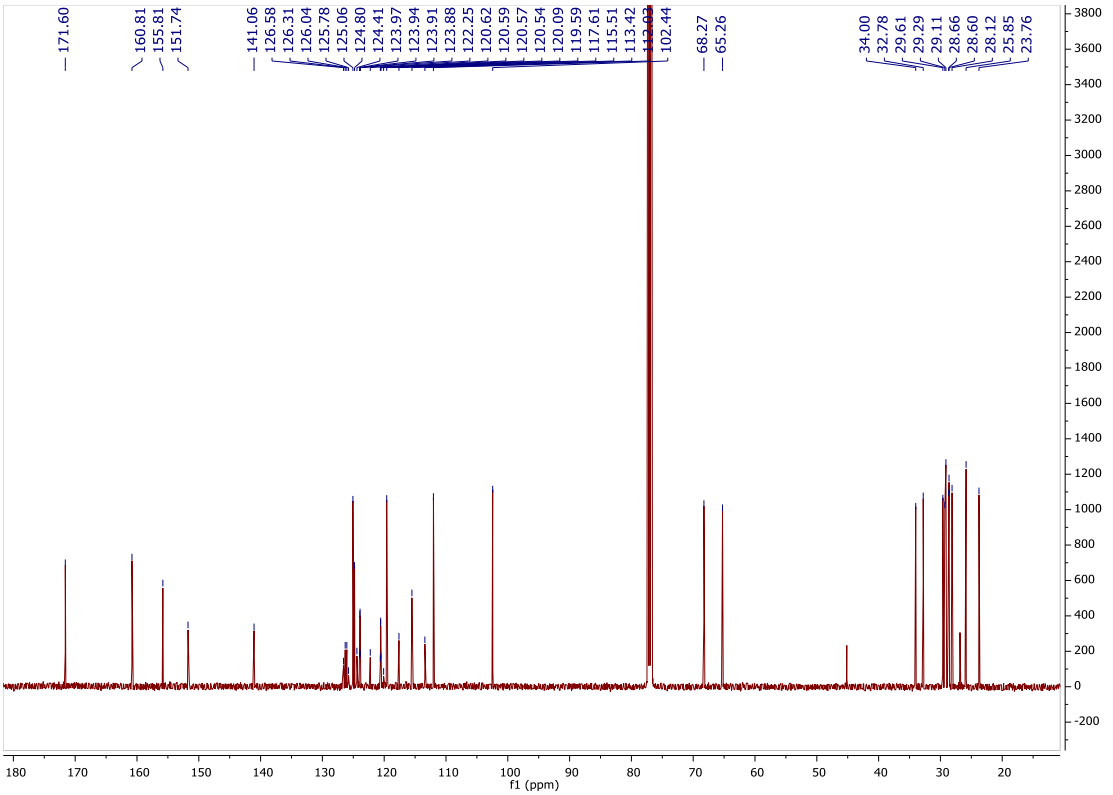
^{1}H and ^{13}C NMR data for S4.

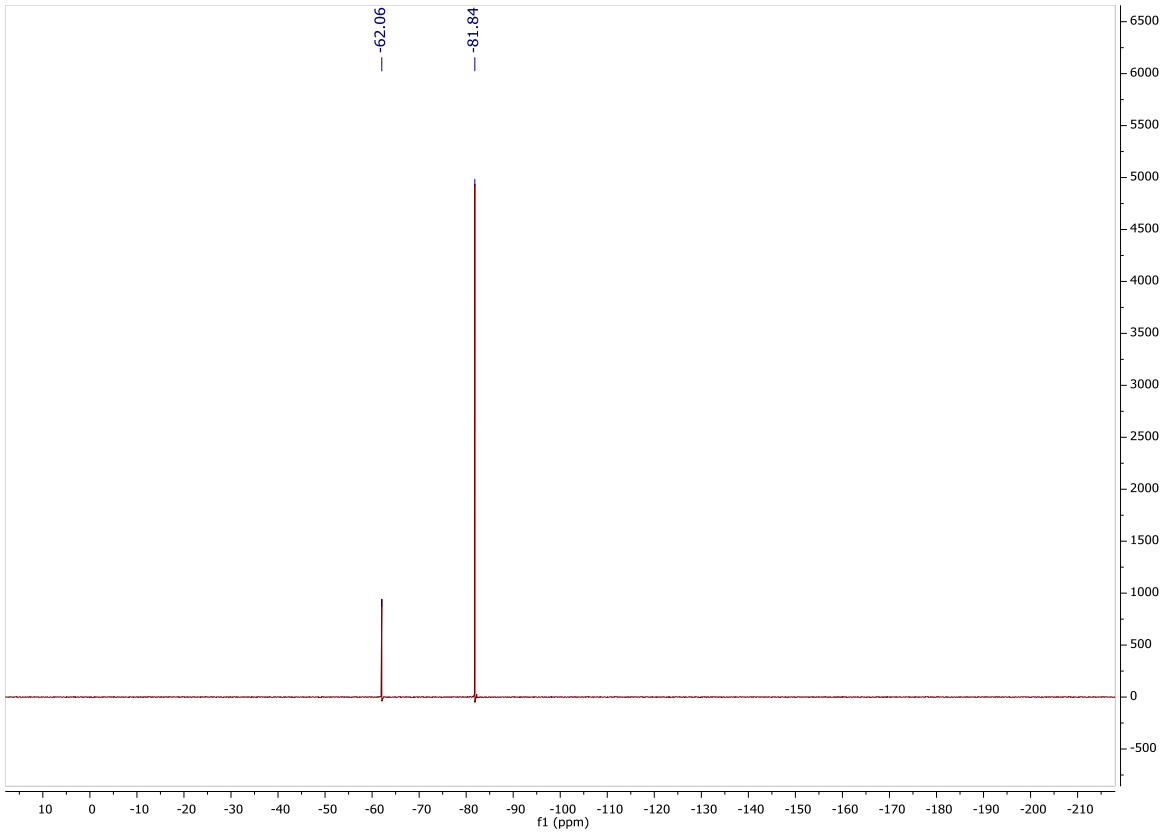




^{1}H, ^{13}C and ^{19}F NMR data for S5.






-62.06
-81.84
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)